Federal/Provincial Research and Monitoring Coordinating Committee (RMCC)

THE 1990 CANADIAN LONG-RANGE TRANSPORT OF AIR POLLUTANTS AND ACID DEPOSITION ASSESSMENT REPORT

Part 4

AQUATIC EFFECTS

1990

ACID RAIN

PLUIES ACIDES

Province of British Columbia
Ministry of Environment and Parks

Gouvernement du Québec
Ministère de l'Environnement

Alberta
ENVIRONMENT

New Brunswick
Department of Municipal Affairs and Environment

Saskatchewan
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Canada

Federal-Provincial Research
and Monitoring Committee (RMCC)

THE 1990 CANADIAN LONG-RANGE TRANSPORT OF AIR POLLUTANTS AND ACID DEPOSITION REPORT

PART 4: AQUATIC EFFECTS

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4.0 INTRODUCTION

4.0.1 SCOPE AND REPORT ORGANIZATION

The 1990 Assessment of aquatic effects related to the long range transport of atmospheric pollutants (LRTAP) has been prepared under the mandate of the Federal-Provincial Research and Monitoring Coordinating Committee (RMCC). As directed by the RMCC, the principal objective of the report is to provide a summary of the present and predicted future status of Canadian aquatic ecosystems as it pertains to development of government policy on acidic deposition. The "policy" orientation of the report is reflected particularly in evaluation of critical SO_4^{2-} loads for sub-regions of eastern Canada which required specification of a biologically relevant threshold criterion for pH. Hence, this Aquatic Effects Report is not a comprehensive review of the state of science, although the focus on Canadian ecosystems does indicate the scale and success of research conducted in Canada over the past decade. References to U.S. and European studies are made only when necessary.

The report is organized according to a series of 4 questions specified by the RMCC and presented at the beginning of each major section below. First, the current state of Canadian aquatic ecosystems is reviewed. The breadth of this subject area required specification of 3 sub-questions. Second, the effect of SO_4^{2-} deposition on lakes is evaluated using water chemistry models leading to specification of critical and target loadings. Third, models are also used to forecast the future condition of Canadian lakes based on 4 realistic SO_2 emission control scenarios; the rate of deterioration or recovery is also discussed. Finally, an evaluation of receptor mitigation (lake and stream liming) is presented.

During the past decade, extensive research has been conducted to determine the physical and chemical processes that regulate interaction between deposition and biogeochemical receptors. It is the degree of interaction that ultimately controls aquatic chemistry and biological effects. Due to the emphasis in this report on assessment of current status and critical load and scenario predictions, the process research is not summarized per se. It should be noted, however, that model development and present understanding of the finer detail of acidification effects has depended on this research.

4.0.2 CONTRIBUTOR ACKNOWLEDGEMENT

The Aquatic Effects Subgroup (AESG) of the RMCC assembled a writing team to produce this report. Included within the team were D.S. Jeffries and J. Dupont (Federal and Provincial Cochairpersons of the AESG respectively), P.J. Blancher, P.J. Dillon, V. Glooschenko, J.M. Gunn, D.C.L. Lam, L.J. Lechner, K.H. Mills, W.D. Watt, and N.D. Yan. While these individuals deserve primary credit for authorship of the Aquatic Effects Report, many other individuals contributed as well. They included: A.G. Bobba, W.G. Booty, A.S. Fraser, R.J. Hall, R.G. Helie, L.M. Johnston, C.K. Minns, F. Norouzian, A.M. Scheuhammer, R.L. Thomas, M.A. Turner, I.Wong and J.A. Wood. The AESG is most appreciative of the dedication and effort provided by all of these scientists.

4.0.3 REVIEW ACKNOWLEDGEMENT

An external peer review of the Report was performed by H.M. Seip and I.H. Muniz from Norway, C. Neal and S.J. Ormerod from the U.K., and J.P. Baker and another reviewer from the U.S.A. who wished to remain anonymous. The principal authors wish to acknowledge the thorough review and constructive comments offered by all of these eminent scientists. The Report has also benefited from reviews performed by several Canadian scientists, particularly J-Y Charette, B. Coker, T.A. Clair, F.C. Elder, H. Hirvonen, W. Keller, I. Kettles, M. Papineau, W.W. Shilts and E. Wiken.

4.1 WHAT IS THE EXTENT OF CHEMICAL AND BIOLOGICAL DAMAGE TO CANADIAN AQUATIC SYSTEMS DUE TO LRTAP POLLUTANTS?

This question contains the assumption that atmospheric deposition of acidifying substances is causally linked to the chemical and biological condition of aquatic systems. However, many biogeochemical and hydrochemical mechanisms contribute to the proton budget of aquatic systems (Munson and Gherini in press) although hypotheses explaining water acidification can be placed within 2 general groups. First, disturbance of the proton budget by introduction of strong acids from external sources (e.g. LRTAP) or triggering of largely dormant, internal geological sources (e.g. mechanical exposure of sulphide minerals during mining, road construction, etc.) can lead to water acidification. When the magnitude of the strong acid introduction is large, the cause-effect linkage is obvious as demonstrated by the presence of acidic lakes in the immediate vicinity of a major SO_2 source (e.g. Sudbury, Ontario, Neary et al 1990) or the many occurrences of acid mine drainage throughout the world. When the magnitude of the strong acid introduction is smaller, the linkage may be partially obscured by operation of natural mechanisms affecting the proton budget of aquatic systems. The challenge to research and monitoring activities over the past decade has been to firmly prove or disprove this linkage. The response is presented in following sections.

The alternative hypothesis explaining water acidification involves vegetation changes typically caused by alteration of land use (Rosenqvist 1978, Krug 1989). Vegetation changes may occur due to either anthropogenic activities (e.g. agricultural or forestry practices) or natural causes (e.g. forest fires). The associated acidification of water systems occurs in response to removal of bases in crops or harvested timber, or incorporation of bases into a rapidly aggrading terrestrial ecosystem. Certainly, historical vegetation changes have affected the acidity of lakes. For example, Delorme et al (1986) concluded that climatic changes account for small variations in the paleolimnologically inferred pH of Batchawana Lake in Ontario prior to 1830, and Elner and Ray (1987) suggest that forest fires may have influenced the historical pH record of some New Brunswick and Nova Scotian lakes. However, most paleolimnological studies conclude that contamination of Canadian lakes by atmospherically transported pollutants began 100-150 years ago, and that the most rapid decreases in inferred pHs have occurred during the last 30-50 years (Charles et al 1990). During this period of rapid pH change, the region of primary concern in Canada (see Section 4.1a.1.2) has not experienced widespread alteration in land use. Therefore, we do not believe that the vegetation change hypothesis is applicable on a regional basis in Canada, although local examples probably do exist.

Evaluation of the current status of Canadian aquatic ecosystems in relation to acidic deposition was divided into 3 manageable portions. The following sections cover chemical effects (4.1a), biological effects related toxicity introduced by ecosystem acidification (4.1b), and biological effects related to contamination of aquatic organisms by certain metals (4.1c).

4.1a WHAT EVIDENCE EXISTS DEMONSTRATING CHEMICAL DAMAGE TO SURFACE OR SUBSURFACE WATER SYSTEM?

4.1a.1 TERRAIN CONSIDERATIONS AND SURFACE WATER RESOURCES

Summary: Forty-three percent of Canada's land area is sensitive to acidic deposition. These sensitive areas generally correspond to the Canadian Shield. The coincidence of sensitive terrain and elevated acidic deposition defines the area of primary concern, namely that area east of the Manitoba-Ontario border (roughly 95° W longitude) and south of the 10 $kg.ha^{-1}.yr^{-1}$ wet SO_4^{2-} deposition isopleth (approximated by 52° N latitude). Canada's water resource is immense; 7.6% of the total area is covered by fresh water. A recent inventory of lakes south of 52° N and east of 90° W found 795,579 waterbodies >0.18 ha in area; 53.7% of them are ≤1 ha in size.

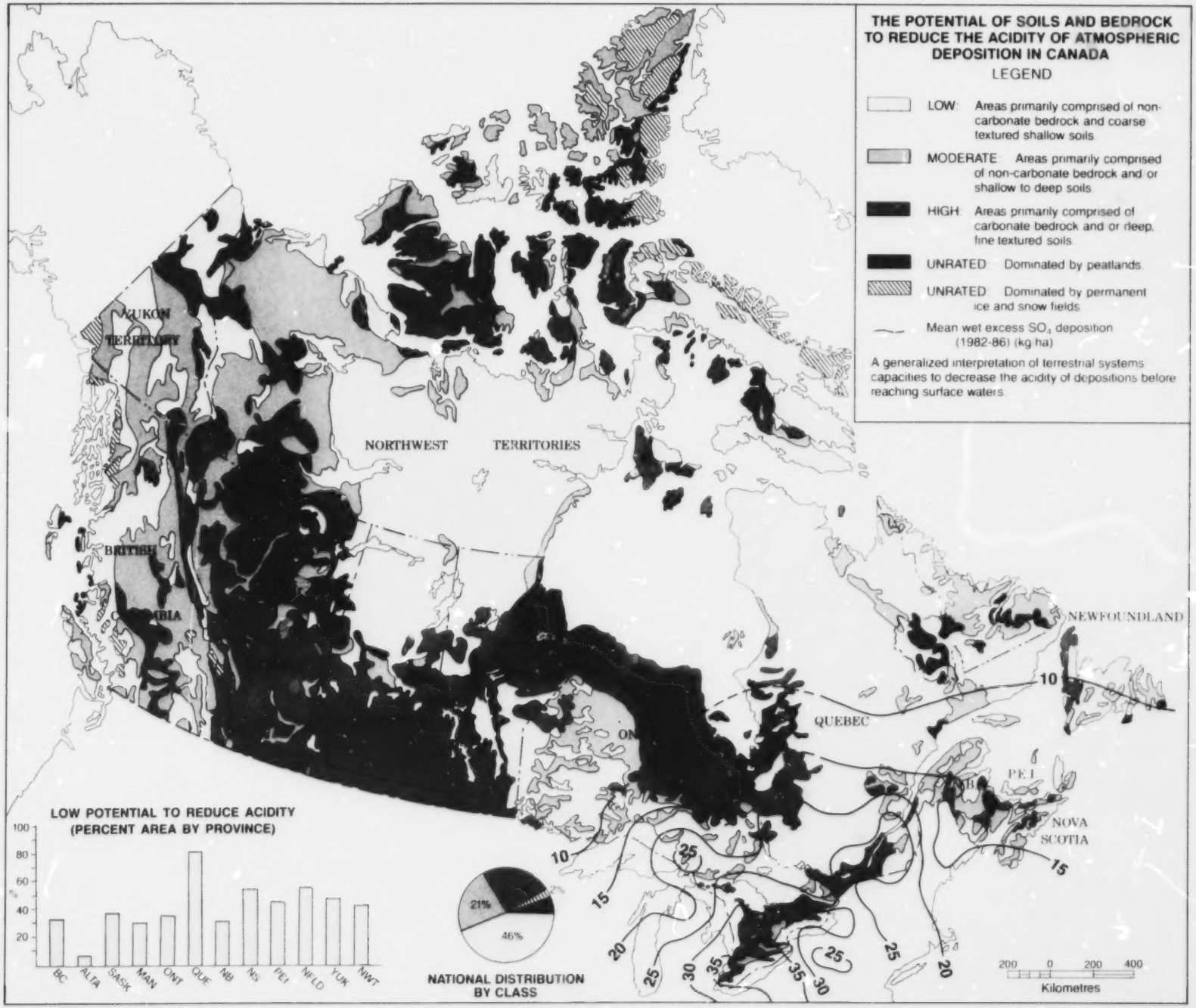
4.1a.1.1 TERRAIN SENSITIVITY

A model has been developed that uses soil and bedrock characteristics to assess the sensitivity of Canadian aquatic systems to acidic deposition (Environment Canada, 1988). Terrain was classified into 3 sensitivity levels by considering bedrock type and properties (mineralogy, texture, and thickness) of the surficial deposits. The terrain class expected to contain the most sensitive aquatic systems (i.e. the one having the lowest potential for reducing precipitation acidity, Figure 4.1a.1) generally has non-carbonate bedrock and coarsely textured, shallow (<1 m) surficial deposits. Furthermore, the glacially derived overburden that predominates in sensitive terrain also has a very limited capacity for SO_4^{2-} adsorption (Rochelle et al 1987).

The model shows that 4 million km^2 (43% of Canada's land area) are sensitive to acidic deposition (Figure 4.1a.1). Large areas of sensitive terrain occur in Newfoundland and Québec, Nova Scotia, northcentral and northwestern Ontario, northern Manitoba and Saskatchewan, western British Columbia, southwestern and northern Yukon Territory, the eastern portion of the District of Mackenzie, the District of Keewatin and much of Baffin Island. These sensitive areas correspond, to a major degree, to the Canadian Shield.

4.1a.1.2 AREA OF CONCERN

Isopleths of average wet SO_4^{2-} deposition (1982-86) in eastern Canada are shown in Figure 4.1a.1. The coincidence of sensitive Canadian terrain and elevated acidic deposition defines the area of primary concern. It is restricted to the southeastern portion of the country, namely that area east of the Manitoba-Ontario border (approximately 95°W longitude) and south of the 10 $kg.ha^{-1}.yr^{-1}$ isopleth (often approximated by 52°N latitude; Kelso et al 1986; RMCC 1986). The southern boundary of Labrador falls at 52°N latitude, while the Manicouagan Reservoir in Québec and Moosonee, Ontario both lie slightly south of 52°N. This assessment concentrates on the area of concern although data evaluation for areas to the north and west are included to provide information under conditions of


THE POTENTIAL OF SOILS AND BEDROCK TO REDUCE THE ACIDITY OF ATMOSPHERIC DEPOSITION IN CANADA
LEGEND
LOW: Areas primarily comprised of non-carbonate bedrock and coarse textured shallow soils
MODERATE: Areas primarily comprised of non-carbonate bedrock and or shallow to deep soils
HIGH: Areas primarily comprised of carbonate bedrock and or deep, fine textured soils
UNRATED: Dominated by peatlands
UNRATED: Dominated by permanent ice and snow fields
Mean wet excess SO_4 deposition (1982-86) (kg/ha)
A generalized interpretation of terrestrial systems capacities to decrease the acidity of depositions before reaching surface waters
YUKON TERRITORY
NORTHWEST TERRITORIES
BRITISH
NEWFOUNDLAND
QUEBEC
PEI
NOVA SCOTIA
10
15
20
25
30
35
LOW POTENTIAL TO REDUCE ACIDITY (PERCENT AREA BY PROVINCE)
100
80
60
40
20
BC
ALTA
SASK
MAN
ONT
QUE
NB
NS
PEI
NFLD
YUK
NWT
21%
46%
NATIONAL DISTRIBUTION BY CLASS
200 0 200 400
Kilometres

lower deposition. Note that wet SO_4^{2-} deposition >10 $kg.ha^{-1}.yr^{-1}$ occurs in southern portions of Alberta and Saskatchewan and southwestern British Columbia (e.g. see 1980 deposition for entire country presented in Environment Canada 1988), but this generally originates as neutral salts (sea salt or terrestrial dust) and/or falls on insensitive terrain.

Most eastern Canadian lakes are hydrologically classified as "drainage" lakes (i.e. lakes having an observable outlet) due to prevailing geomorphological and climatic conditions. "Seepage" lakes (i.e. those without an observable outlet) such as are found in Minnesota, Wisconsin, northern Michigan (Cook and Jager, in press) and Florida (Pollman and Canfield, in press) are rare; for example, very much less than 1% of 6,000 lakes included in an Ontario survey (Neary et al 1990) could be so classified (B. P. Neary, pers. comm.) Therefore, seepage lakes will not receive special consideration here. It is recognized that this class of lakes may exhibit responses to acidic deposition that differ from those dominating in drainage systems.

4.1a.1.3 MAGNITUDE OF SURFACE WATER RESOURCE

Knowledge of the scale of water resources in Canada previously relied on estimates of total lake area presented by geographical unit, for example, by province (Canadian World Almanac, 1989; see Table 4.1a.1), or by drainage basin (Cox, 1978). In order to make such estimates useful for assessing regional effects of acidic deposition, the information has been supplemented by analyses of topographic maps to give estimates of the numbers of lakes (e.g. Kelso et al, 1986). More accurate regional statistics have been generated using GIS technologies (Helie, 1989), but these only consider the total areas of land and water within a drainage basin framework.

Recently, a more accurate surface water resource inventory has been developed for southeastern Canada (16% of the country) using electronic interpretation of satellite images (Helie and Wickware, 1990). The new inventory covers the area south of 52°N latitude (see Section 4.1a.1.2) and east of 90°W longitude (i.e. approximately east of Thunder Bay, Ontario), and includes information on the distribution of lakes according to size and perimeter as well as the total surface area. Note that the inventory area is slightly smaller than the area of concern which extends west to the Manitoba-Ontario boundary, approximately 95°W longitude.

Canada's water resource is immense; 7.6% of the total area is covered by fresh water. The contribution of various size classes of lakes to the overall resource depends on whether numbers or area is considered (see "Inventory" columns in Figure 4.1a.2). For example, lakes >1 ha and ≤ 10 ha in size comprise 35.3% of the numbers but only 8.5% of the areal resource. In contrast lakes >100 ha comprise only 1.2% of the numbers but 71.4% of the area. A subset of the overall population contains 6731 lakes for which both lake area and some chemical information is known (i.e. "Subset" columns in Figure 4.1a.2; see the following section also).

There is an extremely large number of very small lakes (≤1 ha) in southeastern Canada (Figure 4.1a.2). Of the 795,579 waterbodies >0.18 ha in area identified in the new inventory, 53.7% are ≤1 ha. While very small lakes contribute only 1.5% to the areal

Table 4.1a.1 Estimated fresh water resources for Canadian Provinces and Territories. See Figure 4.1a.2 for the distribution of lakes by size and area.

	Freshwater Area(km^2)[1]	Number of Waterbodies[2]
Newfoundland/Labrador	5,690/28,340	138,711/------
Nova Scotia	2,650	6,600
New Brunswick	1,350	3,600
Québec	183,890	899,700
Ontario[3]	86,625	193,100
Manitoba	101,590	57,200
Saskatchewan	81,630	94,000
Alberta	16,800	------
British Columbia	18,070	22,000
Yukon	4,480	------
Northwest Territories	133,300	------
Canada	755,180	------

[1] areas from Canadian World Almanac (1989)
[2] numbers where estimated from Kelso et al (1986) for eastern Canada and Swain (1987) and WNTC (1987) for western Canada; more accurate estimates for the region south of 52°N latitude and east of 90°W longitude are given in Figure 4.1a.2.
[3] freshwater area for Ontario excludes the Great Lakes

extent of the surface water resource, they provide important habitat for many aquatic organisms and waterfowl (McNicol et al 1987). Very little chemical information exists for small lakes (see Section 4.1a.3) although it is known that they predominantly occur in sensitive terrain (Helie and Wickware 1990). Studies relating lake size and chemistry suggest that small lakes tend to have either lower or similar pH and acid neutralizing capacity (ANC) levels compared to larger lakes (see Section 4.1a.2.3).

4.1a.2 AQUATIC DATABASE DESCRIPTION AND CHARACTERISTICS

Summary: A database has been compiled that contains chemical information for 8,505 lakes located in 324 tertiary watersheds across eastern Canada. Very small lakes are greatly under-represented in this database. For assessment purposes, the data were grouped into 22 aggregations of tertiary watersheds. Inferences made using these data will probably under-estimate the magnitude of lake acidification in eastern Canada due to the sampling, lake selection, and statistical procedures used during their collection and compilation. Lake surveys in western Canada have provided less comprehensive data for assessment.

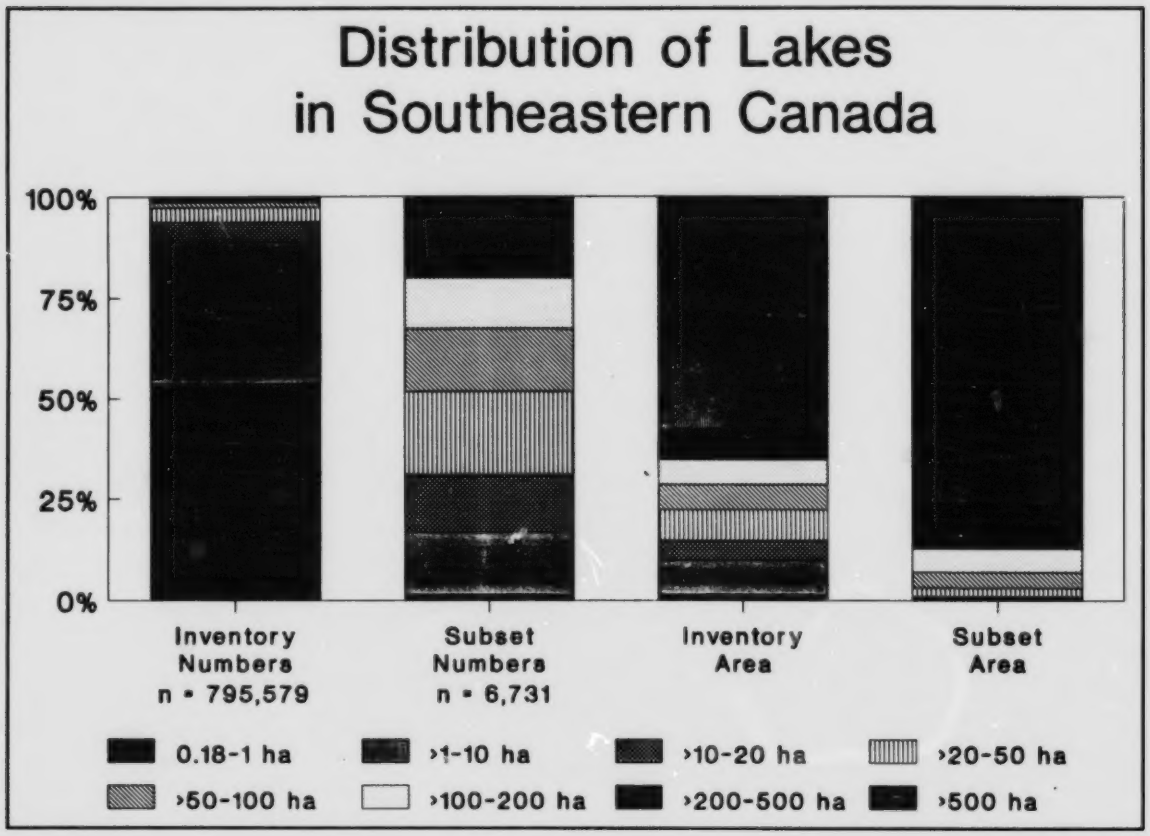


Figure 4.1a.2: Distribution of lakes within specified size classes for the inventory of southeastern Canada (Helie and Wickware 1990) and the subset having some chemical data (Section 4.1a.2). Distributions by both numbers and area are shown.

4.1a.2.1 EASTERN CANADA

Many regional surveys of lake composition have been conducted in eastern Canada over the last decade (e.g. Kelso et al 1986 across eastern Canada; Neary and Dillon 1988 in Ontario; Dupont and Grimard 1986, 1989, and Dupont 1988, 1989, 1990 in Québec; and Howell and Brooksbank 1987 in the Atlantic provinces). In 1985, many of these data were compiled for a limited number of chemical parameters into a single database to permit an interim assessment of the status of eastern Canadian waters (Jeffries et al 1986; Jeffries 1989, in press). In the past year, a new database was assembled by a multi-agency LRTAP Working Group that contains not only more recent survey information but also more chemical and physical parameters than were present in the earlier version (LWG 1989). Results from LWG (1989) will be extensively used for illustrative purposes below. Database characteristics such as data sources, chemical and physical parameters, sampling and analytical methods, editing and quality assurance, protocols for calculated parameters (e.g. organic anions, sea salt corrections, etc.), data

aggregation and storage are presented in LWG (1989).

The database compiled by LWG (1989) contains information for 8,505 lakes (derived from 20,629 individual samples) contained in 324 tertiary watersheds across eastern Canada. The term "tertiary" watershed used here refers to that uniquely defined drainage basin obtained from a third level subdivision of the 4 drainage basins that compose southeastern Canada. In order to obtain geographic units amenable to presentation of spatial variations across eastern Canada, LWG (1989) grouped the data into 22

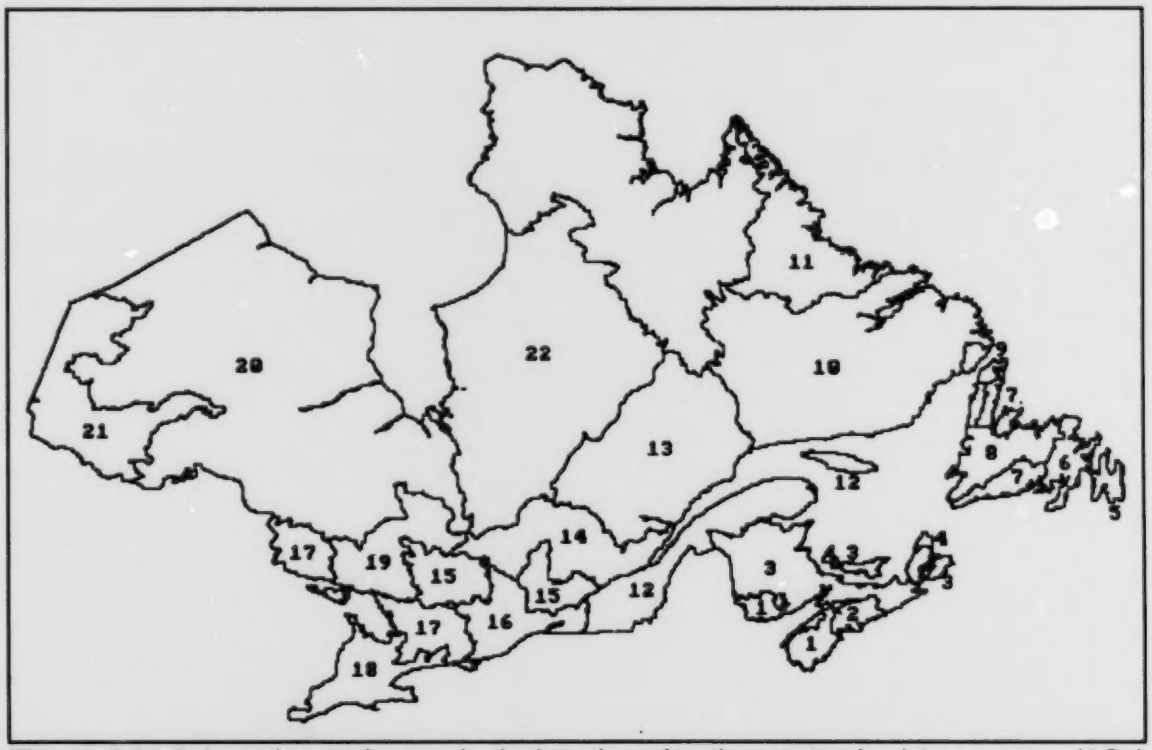


Figure 4.1a.3: Location and numeric designation of tertiary watershed Aggregates (AGs) in eastern Canada used throughout report.

aggregations of tertiary watersheds (Figure 4.1a.3 and Table 4.1a.2). The Aggregates (AGs) were chosen to minimize as far as possible within-group variance and maximize between-group variance by consideration of the spatial variability of lake water specific conductivity. Subjective knowledge of local variability in geology and SO_4^{2-} deposition also played a role in defining AG boundaries. Cluster analyses (Esterby et al 1989) produced similar groupings when applied to the data from the Atlantic provinces.

A large quantity of chemical data also exists for streams and rivers in some areas of eastern Canada. Except for large rivers, most of these data represent drainage to or from nearby lakes. Moreover, since small streams in Canada are frozen part of the year,

many stream fauna spend some time in lakes. Therefore, due to the extended spatial coverage provided by the LWG (1989) database and the inherently lower temporal variability of lake data relative to stream data, the following assessment of surface water status primarily uses information for Canadian lakes. Additional reference to river systems will be noted when appropriate, particularly if they represent an especially important part of the aquatic resource.

4.1a.2.2 WESTERN CANADA (INCLUDING THE TERRITORIES)

Sulphate deposition in most of western Canada is <10 kg.ha^{-1}.yr^{-1}. As noted earlier, exceptions up to approximately 20 kg.ha^{-1}.yr^{-1} occur only in southwestern British Columbia and in southern Alberta and Saskatchewan, and with localized exceptions, these can be attributed to natural sources. Consequently, research and survey activities have been more limited and the data available for assessment are less comprehensive and rarely collected within the context of defining effects of acidic deposition. Lake sensitivity has been determined primarily from survey data for ANC, Ca^{2+}, and/or pH only (Swain, 1987; WNLTC, 1987; Trew, 1988; Lechner and Howard, 1987; Tibbatts et al, 1987). Details of sampling and analytical methodologies are presented in the above references. The quantity of data collected over the last decade and available for assessment of sensitivity varies depending on the parameter and is up to the following: Manitoba - 5813 lakes, Saskatchewan - 420 lakes, Alberta - 982 lakes, British Columbia - 800 lakes, and Northwest Territories - 510 lakes. Spatial coverage is irregular.

4.1a.2.3 DATA REPRESENTATIVENESS

Databases such as those noted above contain data collected using divergent sampling methods and intensities. Moreover, no lake surveys conducted in Canada have been designed to reflect the overall population except one performed recently in southern Québec in which lakes within terrain having no carbonate bedrock were selected to represent statistically the 10-2,000 ha size fraction (Dupont in press). Both of these limitations apply to the database compiled by LWG (1989) which is extensively used below to describe and model the status of eastern Canadian waters.

Jeffries et al (1986) and Jones et al (1990) have considered the implications of making whole population inferences from this sample information. They note that the chemical data are generally "conservative" in nature. That is, the lakes included in the database are either representative of the overall population or biased towards the less sensitive fraction. Inferences will tend therefore to under-estimate the degree of lake acidification. There are several reasons.

First, >80% of the samples represented in the LWG (1989) database were "composite", i.e. collected using either volume-weighting or tube-compositing procedures. Hence, variability introduced by the large natural variations that occur in surface water composition is minimized. Furthermore, most samples were collected during summer, autumn, or winter when ANC is generally at or near its maximum value (P. J. Dillon, unpublished studies). Episodic acidification known to occur in many locations during

Table 4.1a.2 Name of tertiary watershed Aggregates (AG) as defined by LWG (1989), lake numbers and total surface area (km^2) for all lakes >0.18 ha and >1 ha, number of sampled lakes within each AG and their median conductivity and median wet SO_4^{2-} deposition (see also Figure 4.1a.3).

AG No.	Name[1]	Lake Numbers[2]			Total Lake Area[2]		Specific Cond. (μS)	Wet SO_4^{2-} Deposition ($kg.ha^{-1}.yr^{-1}$)
		all	>1 ha	sampled	all	>1ha		
1	S Nova Scotia-New Brunswick	4091	1969	363	1171	1163	28	14.5
2	Mid-eastern Nova Scotia	3258	1825	84	434	428	45	13.7
3	N Nova Scotia-New Brunswick	17588	5357	158	3165	3120	36	13.8
4	Cape Breton Highlands	352	180	33	16	16	26	12.9
5	Avalon	9295	4181	17	514	494	34	9.5
6	E Newfoundland	33650	15736	76	2108	2019	28	8.9
7	N&S Newfoundland	45947	17296	36	1435	1307	18	10.4
8	Central & W Newfoundland	42027	18071	70	7342	7231	24	10.1
9	Belle Isle	14524	5311	8	437	396	79	8.2
10	E Québec - S Labrador[2]	246700	108583	213	16849	16262	11	7.5
11	N Labrador[2]	---	---	52	---	---	10	5.5
12	St. Lawrence S Shore	16920	4487	131	891	846	92	26.9
13	Saguenay[2]	126097	65339	441	17923	17665	21	14.0
14	Laurentide	50959	28972	744	9915	9823	21	20.9
15	SW Québec	45021	22737	761	5950	5858	32	22.9
16	Ottawa Valley	19458	7851	257	3644	3597	47	22.7
17	Central Ontario	57534	23649	2160	5436	5297	32	24.7
18	S Ontario	5947	1812	2	3586	3571	315	>25
19	Sudbury-Noranda	45113	19257	722	7112	7007	39	19.4
20	N Ontario[2]	219981	106412	1450	43895	43437	89	14.9
21	NW Ontario[2]	---	---	625	---	---	33	8.3
22	N. Québec[2]	176165	92147	102	36533	36177	19	15.9

[1] lakes in AG 2, 5, and 19 have local influences; AG 4, 6, and 21 have many coloured lakes.

[2] numbers and areas from the inventory of Helie and Wickware (1990); AG 10, 13, 20 and 22 are partially outside the inventory area and have been areally prorated; AG 11 and 21 fall completely outside the inventory.

spring snowmelt (see Section 4.1a.8) has little expression in the regional database.

Second, the data used here for a given lake are median values when multiple samplings have occurred. One to 4 samples are sufficient to obtain a convergent estimate of whole-lake composition for most ionic parameters when composite sampling is used (Scholer et al submitted).

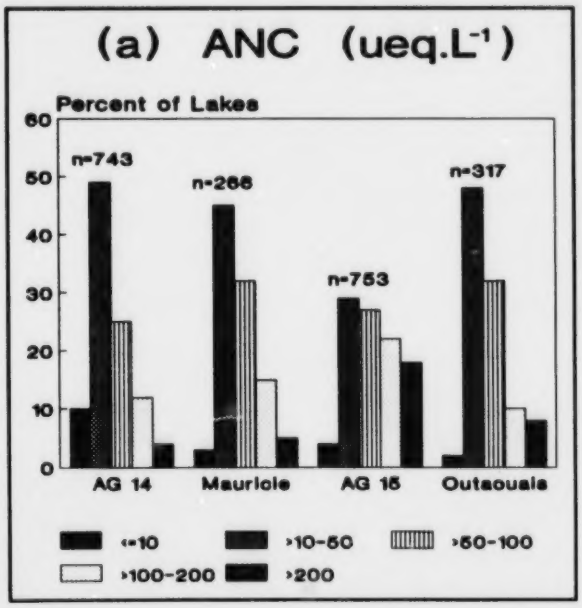
Third, of those sampled lakes where surface area is known (i.e. 6,731), 84% are >10 ha in size. Hence, the database is reasonably representative of the lake population on an areal basis (compare Inventory and Subset Area columns in Figure 4.1a.2) but is non-representative on a numbers basis (i.e. very small lakes are greatly under-represented). Various studies suggest either that smaller lakes tend to have lower pH and/or ANC (e.g. Krester et al 1989) or that there is little relationship between lake size and ANC (e.g. Kelso et al 1986). Neary et al (1990) estimate that 2.5% of Ontario lakes in the 1-9.9 ha size fraction have pH<5.0 compared to 0.9% for lakes 10-99 ha in size. For lakes >10 ha in the Mauricie and Saguenay regions of Québec, a poor ($r=0.3$) but significant direct relationship exists between size and pH (Dupont 1989, 1990), but there is no relationship with ANC. The most comprehensive analysis of size-acidity relationships was conducted by Krester et al (1989) for 1,500 lakes (≥0.2 ha) in the Adirondack Lake Survey. Their results showed that median pH was lower in smaller lakes. Only 1 case has been observed wherein a positive relationship exists between lake size and acidity (A.H. El-Shaarawi, pers. comm.).

Fourth, of the 8,505 lakes in the LWG (1989) database, approximately 6,000 are located in Ontario. The data were collected during approximately 40 individual surveys (for details of the Ontario data, see Neary et al 1990). The rationale for lake selection in some of the individual Ontario surveys and biases inherent in the selection criteria (e.g. required to have good sport fish populations) suggest that, if anything, non-sensitive and non-affected lakes were over-emphasized (Neary et al 1990). Very small lakes were largely excluded as well. On the other hand, a high proportion of the overall population was sampled in some regions of Ontario (particularly south-central Ontario and the region surrounding Sudbury); accurate estimates of population characteristics can be made from this sample information.

AG 14 and 15 enclose the Mauricie and Outaouais sampling region of Dupont (in press). It is therefore possible to compare the non-random data of LWG (1989) to those collected within Dupont's statistically designed survey (Figure 4.1a.4). Dupont's survey excluded lakes located on that spatially limited terrain having calcareous soils or bedrock (providing a small bias to more sensitive systems) and included only those lakes >10 ha in area (perhaps providing a compensating bias to less sensitive systems). The LWG (1989) data compilation contained no similar terrain related or lake size restrictions. The AG14 - Mauricie pair are geographically similar while AG 15 is significantly larger than Outaouais including 3 tertiary watersheds in east central Ontario. The distribution of data for ANC and SO_4^{2-} is visually similar for the AG14 - Mauricie pair implying that extrapolation of sample information from LWG (1989) to the overall population should give reasonable inferences, at least for lakes that are located on sensitive terrain and >10 ha in area. The AG15 - Outaouais pair appear to exhibit greater differences (AG15 distribution shifted to

higher ANC and SO_4^{2-}) that are readily explained by the differing geographical coverage.

In order to obtain a more quantitative analysis of the degree of comparability, a Chi-squared test was applied to the Dupont-LWG dataset pairs. Prior to statistical analysis, the 2 databases were made completely independent by removing the Dupont data from the LWG database which normally contains them. Both datasets were log-normally distributed, and the distributions of ANC, SO_4^{2-}, and Ca^{2+} (the only parameters tested) were similar at the 5% level. A Kolmogorov-Smirnov test was applied to test agreement between the datasets and confirmed the visually-derived interpretation presented above, i.e. the AG 14 - Mauricie pair can be regarded as having the same common distribution while some differences exist between the AG 15 - Outaouais pair. The comparability of the AG 14 - Mauricie pair and the higher ANC present in AG 15 relative to Outaouais suggests that inferences made using the LWG (1989) database will not over-represent the degree of acidification present in these areas.



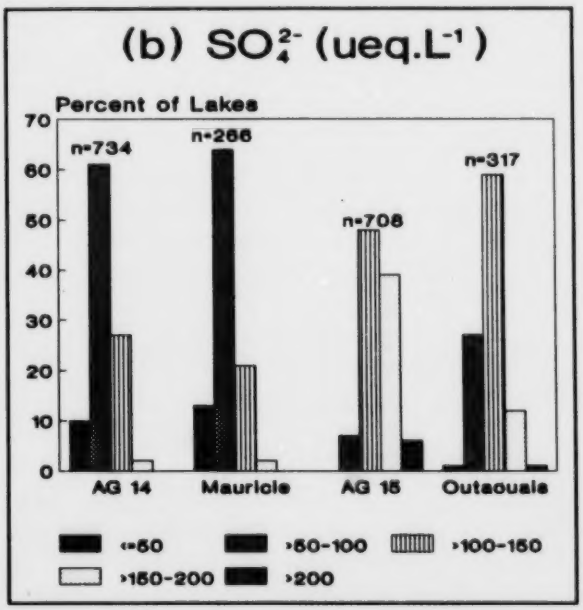


Figure 4.1a.4: Comparison of the LWG (1989) and Dupont (in press) distributions of ANC and SO_4^{2-}* for 2 regions in southwestern Quebec.

While the degree of representativeness of the LWG database no doubt varies from region to region, we contend that the strong bias towards larger lakes, data collection and compilation methods, and the minimal occurrence of episode data within the database will yield inferences that will not over-estimate the degree of lake acidification, i.e. inferences that are conservative in nature. Jones et al (1990) reached a similar conclusion noting that the data subset from Nova Scotia is the only one in which sensitive and acidified lakes may be over-represented. In order to deal with this possibility, they made the assumption the Nova Scotia data only represented sensitive areas of that province (see Figure 4.1a.1) and the remaining areas

were not affected at all. Spatial stratification of the Nova Scotia data into 3 tertiary watershed AGs that have differing terrain characteristics and sampling density (see Table 4.1a.2 and Figure 4.1a.3) addresses this problem directly.

4.1a.3 SURFACE WATER STATUS - EASTERN CANADA

Summary: Lakes in the Atlantic provinces and Québec generally have lower sea-salt corrected base cation (C_b*) and ANC concentrations than those in Ontario primarily due to differing terrain characteristics, and in particular, the irregular occurrence of carbonate minerals in either the bedrock or glacial overburden. Thus Atlantic and Québec region lakes are expected to be more sensitive to acidic deposition; they are also more sensitive than most lakes in the eastern U.S.A. Except for regions containing large emitters of SO_2 such as exist at Sudbury, Ontario and Noranda, Québec, the Atlantic provinces contain the highest proportions of acidic lakes (defined by ANC≤0). Since the database used for this assessment likely will not over-estimate the magnitude of the acidic surface water resource, there are probably >14,000 acidic lakes >1 ha in size (and >31,000 acidic lakes >0.18 ha in size) within that part of south-eastern Canada south of 52°N latitude and east of 90°W longitude.

Sea-salt corrected sulphate (SO_4^{2-}*) concentrations in eastern Canadian waters are primarily controlled by the magnitude of SO_4^{2-} deposition since the glacially derived soils typical of the area possess little capacity to adsorb additional SO_4^{2-} at current deposition levels, and natural sources of S (i.e. sulphide minerals in the bedrock) make little contribution. Hence, the highest median SO_4^{2-}* levels in lakes coincide with the highest deposition (i.e. central and southern Ontario, and southern Québec), and the lowest occur in northern Labrador where deposition is also lowest.

Natural production and dissociation of organic acids supplies a rather uniform acid load to lakes in most areas of eastern Canada. The ANC demand imposed by organic acidity serves to increase the sensitivity of waters to anthropogenic acid inputs and is at least in part the reason why sensitive waters in the Atlantic provinces (i.e. having very low C_b*) exhibit a higher proportion of acidic systems. However, organic acids also buffer against pH reductions in low pH waters (~4.5). Regional acidification of eastern Canadian lakes is primarily due to SO_4^{2-} deposition, not organic acids, a conclusion further supported by consideration of cation-anion ratios.

The contribution of N deposition to acidification of Canadian waters is presently small. Total Al concentrations exhibit narrow distributions at low levels of little concern; however, episodic acidification may yield higher NO_3^- and Al levels over the short term.

The current status of the chemistry of eastern Canadian lakes presented below will focus on the sea-salt corrected sum of base cations ($C_b^* = Ca^{2+}* + Mg^{2+}* + Na^{+}* + K^{+}*$), ANC, sea-salt corrected sulphate (SO_4^{2-}*), organic anions (A^-), NO_3^-, and total Al. Note that sea-salt correction (denoted by * as above) was performed for all tertiary basins that receive significant deposition of marine salts; however, where such a correction would be trivial,

the cation and SO_4^{2-} values were used directly as if corrected. This was particularly important for the Ontario subset in which Cl^- is typically missing. The inability to perform the trivial sea-salt correction in Ontario would remove many data from the following analysis. The ANC data used to describe current status were measured directly using Gran or equivalent procedures. While pH is the parameter of greatest biological relevance (see Section 4.1b), pH measurements in the database tend to be uncertain due to variability in the PCO_2 of the lake water samples. The interpretation of chemical status using pH does not differ greatly from that using ANC; consequently, it will not be included here. The term "acidified" used in this report implies loss of lake water ANC relative to that occurring under background SO_4^{2-} deposition. The term "acidic" implies that ANC is $\leq 0\ \mu eq.L^{-1}$; hence, a lake may be acidified, but not yet acidic.

The distribution of each chemical parameter has been determined for all lakes within the Aggregates (AGs) as specified in Figure 4.1a.3 and Table 4.1a.2 (LWG, 1989). Note that AGs 5, 9, and 18 each contain an extremely small amount of data and are not included in the following discussion. In order to demonstrate the spatial differences that occur across eastern Canada, the data distributions will be presented as "box plots" (e.g. Figure 4.1a.5) which display the 10^{th}, 25^{th}, 50^{th}, 75^{th}, and 90^{th} percentiles for the AGs arranged from approximately west to east. The geographic pattern presented in the box plot figures roughly follows a concave crescent drawn from the low deposition AG 21 in NW Ontario to the low deposition AG 11 in N Labrador. The numbers appearing at the top of each plot indicate the sizes of the sampled lake populations represented by each box. Median concentrations for the samples lakes are given in Table 4.1a.3.

4.1a.3.1 BASE CATIONS (C_b*) AND ACID NEUTRALIZING CAPACITY (ANC)

Lake water C_b* is a reasonable surrogate for "sensitivity" since it reflects the lake basin's capability to neutralize acids through weathering or cation exchange reactions. Ca^{2+}* and Mg^{2+}* generally predominate within C_b* throughout eastern Canada; Na^+* and K^+* represent only a small fraction, e.g. 12 - 18% of C_b* in the Ontario data subset (Neary and Dillon 1988).

Jeffries et al (1986), Cook et al (1988) and Jeffries (in press) have observed that eastern portions of Canada have generally lower C_b* concentration than those in Ontario (top portion of Figure 4.1a.5), a pattern also reflected in the ANC distributions (bottom portion of Figure 4.1a.5). The large variability observed between and in some cases within AGs is controlled by variability in terrain characteristics, particularly in overburden depth and irregular occurrence of carbonate minerals in either the bedrock (southern Ontario, Ottawa R. valley, St. Lawrence R. south shore, and portions of New Brunswick, Newfoundland, and central Nova Scotia) or surficial deposits (influence most apparent in Ontario; Coker and Shilts 1979, Shilts 1981; Hornbrook et al 1986; Kettles and Shilts 1989; Shilts and Kettles 1989). Even subtle differences in base cation and ANC concentrations in the Outaouais and Mauricie subregions of southwestern Québec (AGs 15 and 14) are explained in this manner (Dupont in press). Hence, LWG (1989) found that C_b* and ANC concentrations for AGs influenced by carbonate geology (AG 3, 12, 16, 20, 21, and to a lesser extent 8 and 22) span a wide concentration range, and all possess

Table 4.1a.3 Median concentration for C_b*, ANC, SO_4^{2-}, and A^- from sampled lakes within tertiary watershed AGs in eastern Canada (LWG 1989). The percentage of acidic lakes (ANC≤0) within the sample population is shown also.

Aggregate Number	C_b* $\mu eq.L^{-1}$	ANC $\mu eq.L^{-1}$	SO_4^{2-} $\mu eq.L^{-1}$	A^- $\mu eq.L^{-1}$	ANC≤0 %
1	77	18	53	21	19
2	102	13	73	18	9
3	154	74	54	21	1
4	40	2	17	19	36
6	108	62	38	41	0
7	67	15	30	19	19
8	126	61	47	27	6
10	72	34	30	24	1
11	75	85	15	11	0
12	585	568	114	22	0
13	151	57	52	27	1
14	165	43	83	23	1
15	257	78	146	20	1
16	313	208	134	23	0
17	230	62	150	19	4
19	234	33	208	13	24
20	1024	641	90	37	1
21	338	188	67	63	0
22	190	87	62	38	2

an extended high concentration tail in their distributions. Median C_b* and ANC for lakes in these AGs range from 154-1,036 and 74-641 $\mu eq.L^{-1}$ respectively (Table 4.1a.3), and therefore, they are not particularly sensitive to acidic deposition.

By comparison, concentration distributions for the remaining AGs little influenced by carbonate geology span a narrow range (Figure 4.1a.5) and possess median values that imply greater sensitivity to acidic deposition (40-257 and 2-92 $\mu eq.L^{-1}$ for C_b* and ANC respectively). This is particularly true of lakes in the Atlantic provinces (excluding the less sensitive AG 3; Howell and Brooksbank, 1987); in fact, 19-36% of the LWG (1989) sample population in AGs 1,4, and 7 is acidic (i.e. ANC≤0; see Table 4.1a.3). All receive >10 $kg.ha^{-1}.yr^{-1}$ wet SO_4^{2-} deposition. In contrast, Northern Labrador (AG 11) which is both very sensitive (median conductivity = 10 μS) and receives deposition <10 $kg.ha^{-1}.yr^{-1}$ has no acidic lakes and the highest median ANC of all Atlantic region waters. Sudbury-Noranda (AG 19) contains a high percentage of acidic lakes, many due to the effect of local SO_2 sources.

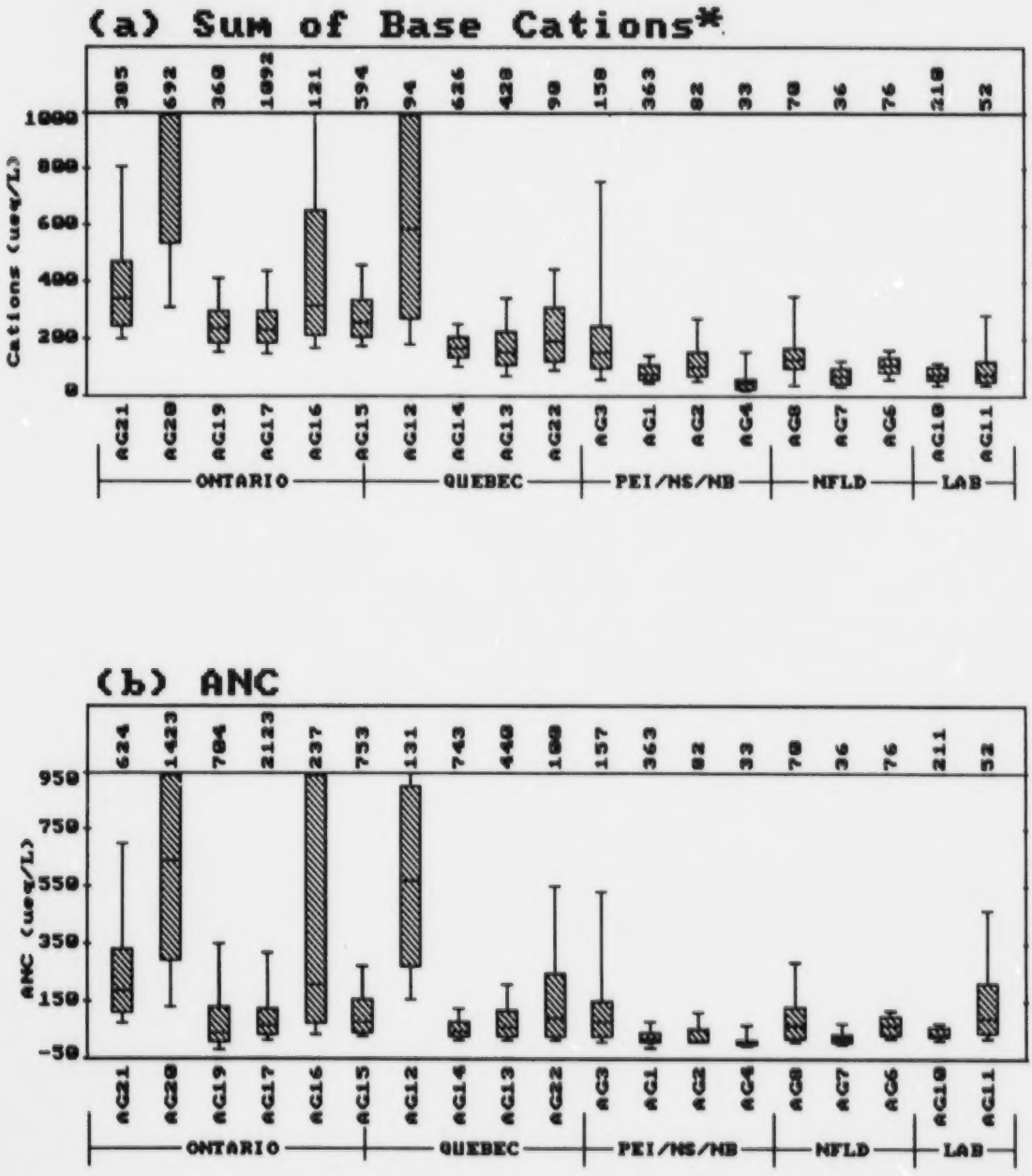


Figure 4.1a.5: Box plot distributions of (a) C_b* and (b) ANC for tertiary watershed AGs in eastern Canada. See text for descriptive details of the box plot and Figure 4.1a.3 for AG locations.

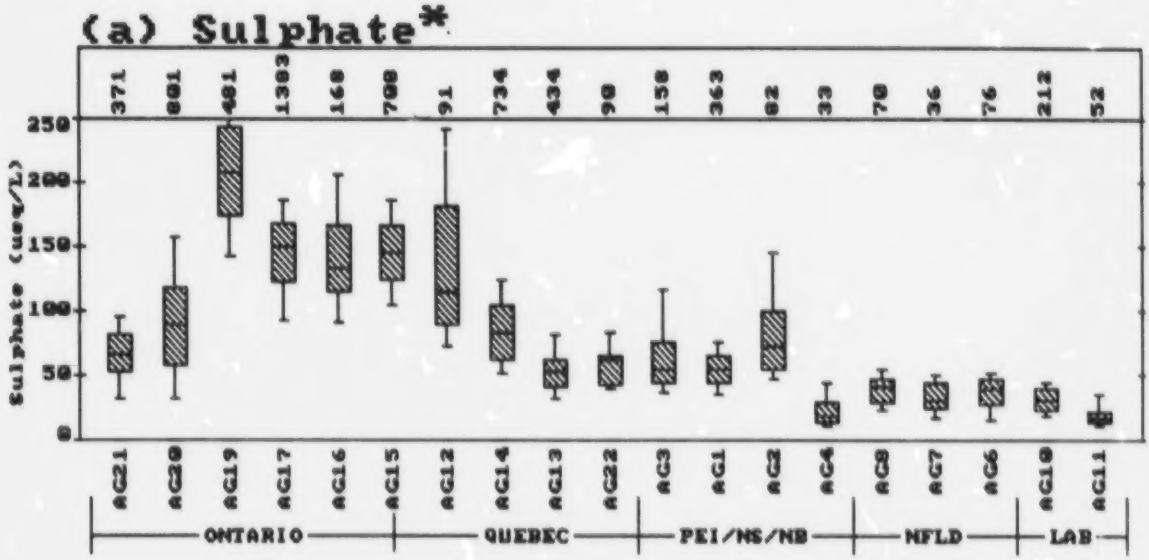
The percentages of acidic lakes in Table 4.1a.3 may be expressed in terms of numbers using the lake resource inventory (Table 4.1a.2) bearing in mind that the sample population is not a statistical subset of the overall population but nevertheless probably under-represents those systems most likely to be sensitive (see Section 4.1a.2.3). Given this qualification, there are >14,000 acidic lakes >1 ha in area (>31,000 lakes >0.18 ha in area) within that portion of Canada south of 52°N latitude and east of 90°W longitude (16% of the country). The magnitude of these estimates seems reasonable. Neary et al (1990) estimate that the number of acidic lakes in Ontario is 7,250 based on a sample population of 6,000 lakes of which over 99% are >1 ha in size. In southern Québec (south of 51°N latitude, north of the St. Lawrence River, and west of 62°W longitude), statistical extrapolation from an overall population of 31,800 lakes in the 10-2,000 ha size fraction gives 5,993 lakes with pH≤5.5 (J. Dupont, pers. comm.).

Lakewater concentrations of both C_b* and ANC may be affected by acidic deposition, the former increasing if terrestrial basin export of base cations has increased (i.e. reflected in an F>0; Henriksen 1982, 1984; Wright 1983), and the latter decreasing if the acid input is not completely counteracted by the base cation increase. It is likely that F varies as a function of initial C_b* concentration (Husar et al, in press; Marmorek et al 1990). Those AGs with inherently low C_b* (due to low geochemical weathering rates) will exhibit little change in base cation concentrations due to acidic deposition, and lake acidification occurs as SO_4^{2-} replaces ANC (see also Section 4.1a3.5). Even within Ontario where C_b* is relatively higher, 60% of the observed spatial gradient in ANC is linked to replacement of ANC by atmospherically deposited SO_4^{2-} (Neary and Dillon 1988; Neary et al 1990).

Comparison of eastern Canadian and US lake water chemistry (Baker et al, in press; Canadian data used was the database of Jeffries, in press) demonstrates that base cation concentrations (represented by $Ca^{2+} + Mg^{2+}$ only) observed for sampled lakes in Québec and all provinces to the east are similar to and often less than those observed for lake populations in many US subregions (e.g. Adirondack Mountains, Maine, Upper Midwest, Southern Blue Ridge, Florida). Moreover, the percentage of lakes with ANC<200 $\mu eq.L^{-1}$ (87-97%) within these provinces is also higher than that observed in all US subregions except Florida. Similar conclusions were reached by Dupont (in press). These data further attest to the high sensitivity of waters found in Québec and the Atlantic provinces relative to other locations in eastern North America. Ontario waters, particularly those in northern subregions outside local influences within the Sudbury-Noranda AG (19) are sometimes less sensitive (higher C_b* and ANC) than the US subregions presented in Baker et al (in press).

4.1a.3.2 SULPHATE

Sulphate concentrations in eastern Canadian waters are primarily controlled by the magnitude of SO_4^{2-} deposition. This occurs because the glacially derived soils typical of the area possess little capacity to adsorb additional SO_4^{2-} at current deposition levels (Rochelle et al 1987), and natural sources of S (i.e. sulphide minerals in the bedrock) make little general contribution (Wright 1983; Caron 1984; Neary and Dillon 1988; Clair et al 1989a). Hence, LWG (1989) found that the highest median SO_4^{2-} concentrations



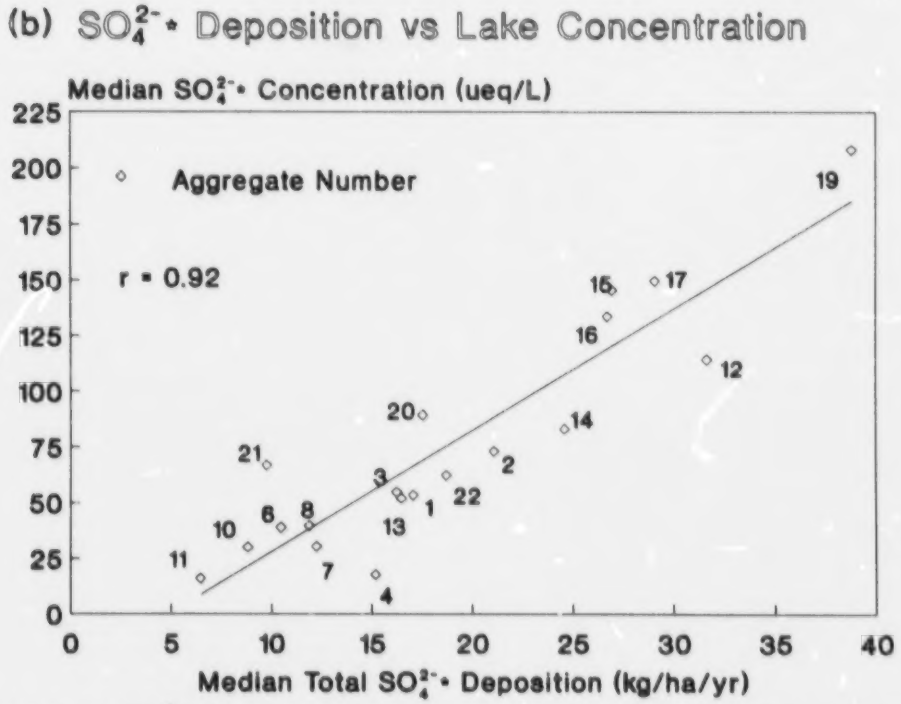


Figure 4.1a.6: (a) SO_4^{2-}* box plot distributions for eastern Canadian AGs; (b) relationship between median total SO_4^{2-}* deposition and median lake concentrations.

occur in those areas receiving the highest deposition, i.e. central and southern Ontario, and southern Québec (AG 12, 14-19, see top portion of Figure 4.1a.6 and Table 4.1a.3; median lakewater SO_4^{2-} ranges from 83-208 $\mu eq.L^{-1}$). This agrees with earlier conclusions by Jeffries et al (1986), Cook et al (1988), and Jeffries (in press). In contrast, most portions of the Atlantic Provinces (e.g. AGs 1, 3, 6, 7, 8, 10; exceptions noted below) receive moderate deposition and have median lake concentrations of 30-54 $\mu eq.L^{-1}$. Northern Labrador which receives the lowest deposition has a lake water median of only 15 $\mu eq.L^{-1}$. A plot of SO_4^{2-} deposition vs lake concentration gives a noisy positive relationship when considered on a lake-by-lake basis. This is as expected given the variability in processes that influence each individual; however, the relationship between median total SO_4^{2-} deposition (i.e. wet + estimated dry) and median lake concentration for eastern Canadian AGs is more obvious and highly significant (bottom portion of Figure 4.1a.6). Similar observations of this general relationship exist even within subregions of eastern Canada, e.g. Neary and Dillon (1988) in Ontario, Dupont and Grimard (1986, 1989) in southern Québec, and Howell and Brooksbank (1987) in the Atlantic provinces.

Exceptions arise and are apparent in the LWG (1989) database due to localized influences such as major smelter sources (i.e. Sudbury-Noranda, AG 19) and power plant and anthropogenically disturbed geological sources (i.e. AG 2). They lead to SO_4^{2-} distributions which are shifted to higher concentrations relative to those in neighbouring AGs which presumably receive comparable deposition from long range sources. Conversely, extensive wetlands in the Cape Breton Highlands (AG 4) adsorb input SO_4^{2-} (see Section 4.1a.5) yielding a relatively lower median value. AG 12 covers the St Lawrence R. south shore and spans a particularly wide range in deposition due to its location and elongated shape; it therefore also exhibits a wide distribution in lakewater SO_4^{2-} concentrations. In fact, between-lake variability in deposition is probably responsible for some of the dispersion apparent in all the distributions.

In-lake SO_4^{2-} reduction (Schindler 1986) could confound the deposition-lake concentration relationship (i.e. yielding lower lake concentrations than would be expected otherwise), and between-lake differences probably also contributes to the observed dispersion in SO_4^{2-} concentrations. However, the fact that good deposition-concentration relationships are observed ubiquitously suggests that SO_4^{2-} reduction is of minimal importance on a regional basis. Only lakes with long water retention times derive significant benefit (ANC production) from SO_4^{2-} reduction (Schindler 1986; Kelly et al 1987).

4.1a.3.3 ORGANIC ANIONS

Naturally occurring organics are a heterogeneous and complex mixture of solutes: fulvic acids, humic acids, carbohydrates, carboxylic acids, amino acids, etc. (Thurman 1985). The H^+ dissociation constants (pK_a) of these solutes vary over a wide range. Some are weak acids having $pK_a > 5$ and these will have little effect on the acidity of natural waters. Others are moderately strong acids with $pK_a < 4$, and in waters of circumneutral pH, their dissociation depresses ANC. In waters having $pH < 5$, these acids buffer H^+ concentrations.

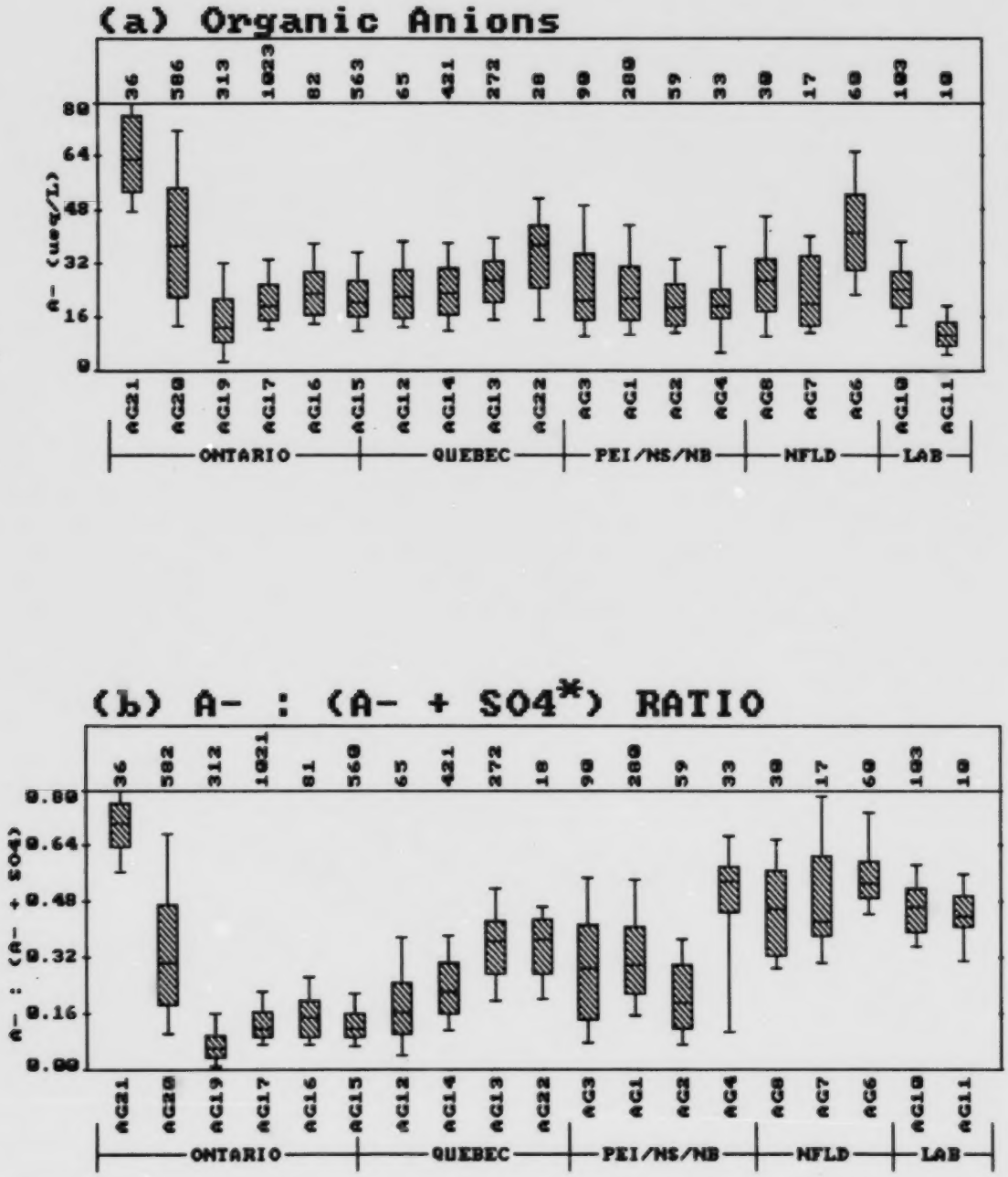


Figure 4.1a.7: Boxplot distributions for (a) A^- and (b) the ratio $A^-:A^- + SO_4^{2-}$* for AGs in eastern Canada.

The effect of organic acids on the chemistry of eastern Canadian lakes is assessed by considering organic anion (A^-) concentrations (top panel of Figure 4.1a.7 and Table 4.1a.3). The A^- concentrations were calculated using the method of Oliver et al (1983) except that the contribution of DOC to A^- was set at 5 rather than 10 $\mu eq.mg^{-1}$ DOC (Wright 1989; Kortelainen et al 1989). The A^- calculated in this manner probably reflectsonly the ionic form and not that bound to Al, Fe, etc. Driscoll et al (1989) calibrated the Oliver et al model using data from the U.S. Eastern Lake Survey and found that at low pH, the model over-predicts A^- while at high pH, the reverse is true. Urban et al (1989) summarized the charge density of various water types; surface waters, streams and lakes had mean charge densities of 2.6-10.1 $\mu eq.mg^{-1}$ C. The use of a single charge density (i.e. 5 $\mu eq.mg^{-1}$ DOC) for all lakes in eastern Canada is a simplification that must be considered when interpreting the influence of organic acids.

LWG (1989) found that for all AGs except E Newfoundland, N Ontario, NW Ontario, and N Québec (AG 6, 20, 21, 22), A^- distributions are similar in breadth with median values falling in a narrow range (11-27 $\mu eq.L^{-1}$) compared to many other major ions. AG 19 (Sudbury-Noranda) which is most affected by a local SO_2 source, has one of the lowest A^- medians. Natural production and dissociation of organic acids is supplying a rather uniform H^+ load to lakes in 15 of 19 eastern Canadian AGs. The 4 exceptions noted above have higher A^- medians (37-63 $\mu eq.L^{-1}$), and 2 of them (i.e. 20, 21) have broader distributions as well (Figure 4.1a.7). Natural acidification of lakes in these 4 AGs may be of greater significance although only 0-2% of their sampled lakes had ANC$\leq$0 (Table 4.1a.3). Dupont and Grimard (1989) have shown that highly coloured lakes in southern Québec have lower pHs than clear lakes. However, in Ontario and over all of eastern Canada, no relationship exists between low pH and/or ANC and high A^- in lakes (Neary and Dillon 1988; Jeffries et al 1986).

Bearing in mind the implications of using a single charge density value in the Oliver et al (1983) model, the relative significance of A^- and SO_4^{2-} contributions to lake acidification was assessed by LWG (1989) using the ratio $A^-:(A^- + SO_4^{2-}*)$ (see bottom panel of Figure 4.1a.7). A ratio value of 0.5 indicates an equal contribution and 0.25 a 3-fold greater contribution by SO_4^{2-}. Since lake water A^- concentrations exhibit a small spatial variation compared to SO_4^{2-}, this ratio varies in an inverse manner to SO_4^{2-} (compare with Figure 4.1a.6). Hence, low ratio values in southern Ontario and Québec (usually <0.25 for AG 14-19) reflect high lake water SO_4^{2-} due to deposition. Even if the higher charge density value is used to calculate A^- for these AGs, the ratio will seldom exceed 0.5. Higher ratio values the Atlantic provinces (particularly Newfoundland and Labrador, AG 6-11 in Figure 4.1a.7b) most probably reflect lower atmospheric SO_4^{2-} inputs, although terrain retention of SO_4^{2-} may be a factor for AGs having extensive wetlands (AG 4). A number of lakes in AG 4-11 have ratio values $\geq$0.5, but the median lake is $\geq$0.5 in only 2 of them (i.e. 4 and 6). As has been concluded in the U.S.A. (Brakke et al 1988; Eilers et al 1988a,b), regional acidification of eastern Canadian lakes is not due to naturally occurring organic acids. A careful analysis of organic acid contributions in other locations purported to have naturally acidic lakes in the absence of acidic deposition also reached the same conclusion (Norton et al 1989).

Evaluation of the organic and SO_4^{2-} acidity in intensively sampled coloured and clear

streams within the Kejimkujik calibrated watershed of southwestern Nova Scotia (e.g. Kerekes et al 1986) showed that anthropogenic SO_4^{2-} increases the free acidity of these waters over that which is naturally present due to organic acids. The dissociation of organic acids at this site creates an ANC demand without reducing water pH to the point that A^- becomes a significant H^+ buffer.

Other evidence suggests that this conclusion applies in a regional context. While sensitive (i.e. low C_b*) lakes that are little influenced by either organic acids or acidic deposition generally exhibit pH>>6 (e.g. 75% of western U.S.A. lakes have pH≥6.8, Baker et al in press), paleolimnological inferences of historical lake pHs in Nova Scotia are somewhat lower (~6, see summary by Charles et al 1990). Similarly, water chemistry models that include consideration of A^- predict that under background deposition, lake pHs in AG 1 spanned a narrow range centred around pH=6 (see Section 4.3.1.1 and 4.2.2). Hence, acidity supplied by organic acids probably accounts for the relatively low historical pH and ANC levels inferred for some Nova Scotian lakes. However, the low C_b* supply to these lakes means that even moderate levels of SO_4^{2-} deposition (e.g. the ~15 $kg.ha^{-1}.yr^{-1}$ currently observed) will reduce lake pH to the point where A^- begins to act as a buffer (<5), and is the reason why sensitive waters in the Atlantic provinces exhibit such a high percentage of acidic systems (Table 4.1a.3).

It is possible that input of acidic deposition may cause a shift in the chemistry of coloured lakes away from acidification by organic acids to acidification by strong acids. Support for this hypothesis is available from Norway (paleolimnology, Davis et al 1985; whole catchment experiments, Wright 1989) and from the negative correlation that is sometimes observed between lake concentrations of SO_4^{2-} and DOC or A^- (Driscoll et al 1989). Canadian lake data are less supportive. With a few exceptions, A^- is evenly distributed across deposition gradients in eastern Canada (Figure 4.1a.7), while both high and low A^- is observed in areas of low deposition, i.e. NW Ontario (AG 21) and N Labrador (AG 11).

4.1a.3.4 NITRATE AND TOTAL ALUMINUM

After S, deposition of N compounds is the next most important class of anthropogenic acids entering aquatic systems in Canada. Growing ecological concern arises from the fact that NO_x emissions are not decreasing in North America and that there is now evidence of N-induced surface water acidification, particularly in Europe (Henriksen 1988, Henriksen and Brakke 1988). The biogeochemical processes of N-induced acidification and observations of the Canadian situation have been reviewed by Dillon and Molot (in press) and are presented in Section 4.1a.7. The regional distribution of NO_3^- observed in Canadian lakes (LWG, 1989) is shown in the top portion of Figure 4.1a.8. Most tertiary watershed AGs (13 of 18) exhibit NO_3^- concentrations <5 $\mu eq.L^{-1}$; of the remaining 5 AGs, two contain substantial agricultural activity (i.e. AG 3 and 12) which can account for the higher concentration distributions, while the others (AG 11, 20, and 22) are all situated in northerly locations outside the area of maximum N deposition. The higher concentrations for these 3 AGs are probably related to terrain and climatic factors rather than deposition. Almost all Canadian lakes have NO_3^- levels that are substantially below those observed in acidified areas of Europe (median of 25 sites was 40 $\mu eq.L^{-1}$, Henriksen

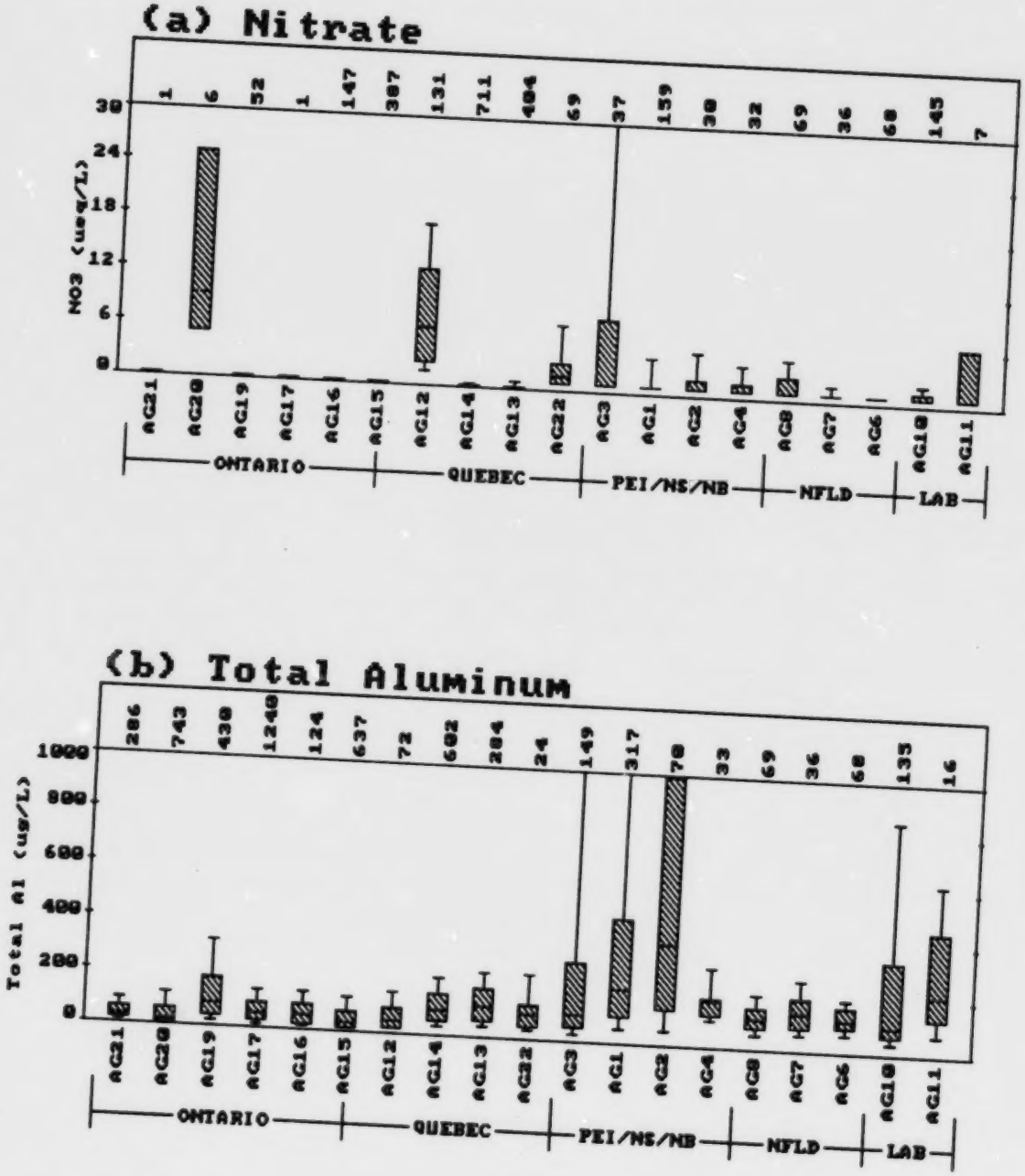


Figure 4.1a.8: Box plot distributions for (a) NO_3^- ($\mu eq.L^{-1}$) and (b) total Al ($\mu g.L^{-1}$) for AGs in eastern Canada.

1988). The contribution of N deposition to acidification of Canadian waters is small at this time. The only North American location exhibiting regionally elevated NO_3^- in lakes is the Adirondack Mountains of New York State (median of 17 lakes was 23 $\mu eq.L^{-1}$, Driscoll and Newton 1985).

Aluminum enters surface water systems by either weak- or strong-acid leaching from acidic soils. Waters from near surface soil horizons have H^+ as the dominant acidic cation. During downward percolation of these waters through intermediate horizons, some H^+ is consumed by primary weathering or ion exchange reactions thereby liberating other cationic species including Al. In lower soil horizons, weathering reactions continue to consume H^+; however, the higher pH that results causes demobilization of Al by either precipitation or adsorption. The Al species and their concentrations observed in surface waters reflect mixing of inputs from these differing soil environments.

Aluminum may be toxic to aquatic biota (see Section 4.1b). Within the aquatic environment, Al exists in a variety of chemical forms; however, it is the inorganic species that are biologically most toxic, particularly in waters with low Ca^{2+} concentrations. Only leaching by strong acids transports ecologically significant quantities of this metal to surface waters (see various papers in Sposito 1989). Hydrological flowpaths are very important in determining Al transport and the relative contribution to surface waters from the various soil environments noted above. Data for inorganic Al is extremely limited in Canada and therefore, the spatial distribution is presented in terms of total Al (Figure 4.1a.8b). Note that total Al is expressed in $\mu g.L^{-1}$ since the wide range of pHs and DOCs observed in Canadian waters makes it problematic to perform a general conversion to $\mu eq.L^{-1}$.

Jeffries and Hendershot (1989) reported stream concentrations in areas affected by acidic deposition in the range 0-828 $\mu g.L^{-1}$ while Driscoll (1989) reported concentrations for lakes of 0-1,130 $\mu g.L^{-1}$ (excluding moorland pools in Belgium having 297-8,100 $\mu g.L^{-1}$). In comparison, total Al for lakes in many Canadian AGs (Figure 4.1a.8b) exhibit rather narrow distributions at low concentration levels (14 of 19 AGs have median total Al $\leq$110 $\mu g.L^{-1}$). Inorganic Al species will have even lower concentrations and thus, it is unlikely that Al will be causing biological effects in most waters from these AGs. The broadest distributions of total Al occur in 5 AGs from the Atlantic provinces. Greater than 25% of sampled lakes in AG 1, 2 and 11 exhibit total Al >400 $\mu g.L^{-1}$, while Ag 3 and 10 have between 10 and 25% in this category. There is a general expectation that low pH correlates with high Al (Driscoll 1989); however, both acidity and elevated DOC levels likely play a role in these AGs. Since Atlantic region waters have generally low C_b* concentrations, biological effects related to Al toxicity may be of greater importance here. Note that total Al >400 $\mu g.L^{-1}$ occurs in AGs 1 and 2 which receive elevated SO_4^{2-} deposition and have experienced fish population losses (Watt et al 1983), and also in AG 11 which receives low deposition and has no reported population losses.

High Al concentrations may be of greater biological concern in streams than in lakes due to the lower availability of refugia within the former. Furthermore, episodic acidification may yield short term surface water concentrations that are of even greater concern (e.g. Sullivan et al 1986; Henriksen et al 1984). Little data exists in Canada for assessment,

however.

4.1a.3.5 ANION-CATION RATIOS

Geochemical concepts expressed in terms of ratios of one or more acid anions to C_b* have been used extensively to assess the spatial extent of surface water acidification (Jeffries 1986, in press; Schindler 1988; see also various papers from Charles in press). Their interpretation depends on the expectation that terrain response to elevated SO_4^{2-} deposition (when not adsorbed by soils as is generally the case in Canada) is reflected in either a surface water loss of ANC (i.e. acidification) or an increase in C_b*. As discussed in Section 4.1a.3.1, it is likely that Canadian waters primarily respond by ANC reduction rather than increased base cation weathering.

The usefulness and limitations of anion-cation ratios have been discussed in detail by Sullivan (in press). In regions receiving little SO_4^{2-} deposition, the ANC:C_b* ratio is typically >0.6 (Schindler 1988) and will be near unity in the idealized case where carbonic acid weathering is the sole driving force supplying ions to surface waters. ANC:C_b* <0.6 suggests that a change in acid-base chemistry has occurred although the influence of both A^- and SO_4^{2-} must be considered when assigning cause, and this ratio on its own, cannot differentiate between acidification and elevation of C_b*. It should be noted that insensitive terrain having high weathering rates (reflected in high water conductivity and C_b*) will maintain high ANC:C_b* independent of deposition. The SO_4^{2-}:C_b* and A^-:C_b* ratios are useful since they aid evaluation of region-to-region differences in acidification, and values >1 (implying that ANC<0) provide unequivocal evidence of acidification by SO_4^{2-} and A^- respectively, although the implication of using the charge density of 5 μeq.mg^{-1} DOC to calculate A^- must be considered.

Simultaneous consideration of the 3 ratios (Figure 4.1a.9) shows that lake acidification is widespread in eastern Canada and that the principal cause is SO_4^{2-} deposition (LWG 1989). For example, 14 of 19 tertiary watershed AGs shown in the top panel of Figure 4.1a.9 have >50% of the sampled population with ANC:C_b* <0.5, and many lakes have extremely low values <0.2. Only AG 11,12, and 20 have ANC:C_b* distributions largely >0.5 due to either low SO_4^{2-} deposition (i.e. AG 11), or high C_b* derived from rapid weathering permitted in less sensitive terrain (i.e. AG 12), or both (AG 20). Relative to C_b*, there is a widespread deficit of ANC in many eastern Canadian lakes.

Data AGs having low ANC:C_b* ratios have SO_4^{2-}:C_b* values that are greater than those typical of low deposition areas (e.g. >0.3, the approximate upper limit for SO_4^{2-}:C_b* observed in AG 11 and 21; see middle panel of Figure 4.1a.9). Two AGs (2,19) have >25% their lakes acidified by H_2SO_4, i.e. SO_4^{2-}:C_b* ratio >1.0. The origin of SO_4^{2-} in both of these areas can be attributed in part to local emissions or geological sources although they also receive deposition originating from long range sources. However, >10% of the lakes in southern Nova Scotia and New Brunswick (AG 1) have SO_4^{2-}:C_b* >1.0; acidification of these lakes can be attributed only to SO_4^{2-} originating from long range sources. Comparison of the top 2 panels of Figure 4.1a.9 clearly demonstrates that an inverse relationship exists between ANC:C_b* and SO_4^{2-}:C_b*. Since SO_4^{2-} concentrations are

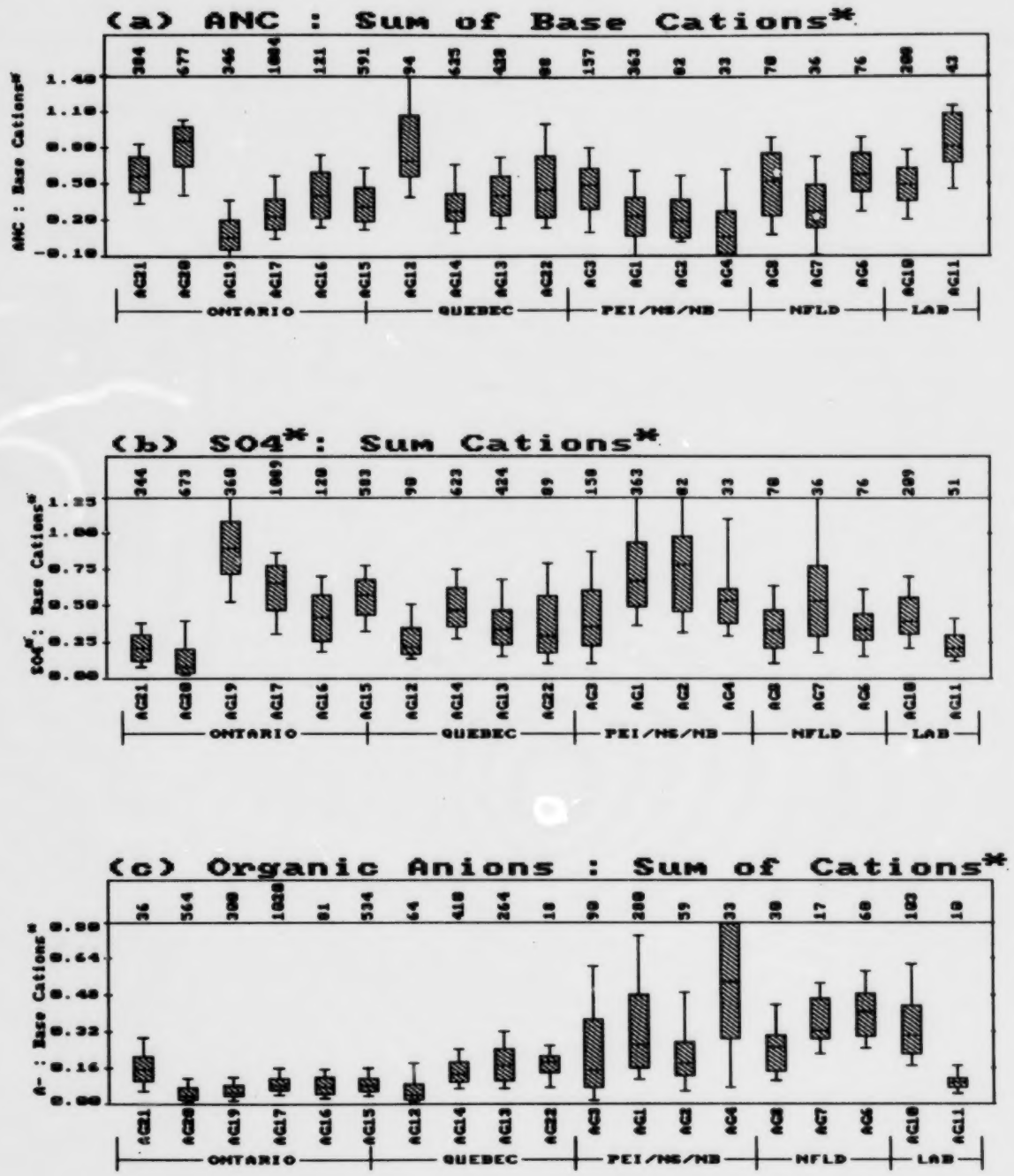


Figure 4.1a.9: Box plot distributions for (a) ANC:C_b*, (b) SO_4^{2-}:C_b*, and (c) A^-:C_b* for AGs in eastern Canada.

strongly linked to deposition (see Section 4.1a.3.2), ANC loss in Canadian lakes is related to atmospheric transport and deposition of anthropogenic SO_4^{2-}.

In contrast to $SO_4^{2-}:C_b^*$, $A^-:C_b^*$ exhibits no relationship with $ANC:C_b^*$. Lakes in the Atlantic provinces (e.g. right hand side of bottom panel of Figure 4.1a.9) generally have higher $A^-:C_b^*$ than those in Ontario and Québec. This is related as much to the low level of C_b^* production in the Atlantic region (Figure 4.1a.5) as it is to higher A^- (Figure 4.1a.7). When 5 $\mu eq.mg^{-1}$ DOC was used for the charge density, there were no lakes in the LWG (1989) database in which $A^-:C_b^*$ exceeded 1.0, i.e. no lakes have been unequivocally acidified by natural organic acids. If the higher charge density of Oliver et al (1983) is used, some lakes in AG 1-4 and 6-10 have $A^-:C_b^*$ exceeding 1; however, it would seem inappropriate to use the higher charge density in the Atlantic region of eastern Canada given the findings of Driscoll et al (1989). As noted previously, the ANC demand exerted by natural organics serves to make Atlantic region waters more vulnerable to further acidification by SO_4^{2-}.

4.1a.4 SURFACE WATER STATUS - WESTERN AND NORTHERN CANADA

Summary: Lakewaters in western and northern Canada exhibit a broad range in sensitivity based on inspection of ANC, Ca^{2+}, and pH data. It is likely that the currently low levels of acidic deposition have not significantly altered water chemistry. The most sensitive areas usually coincide with either the geological formations of the Canadian Shield (Manitoba, Saskatchewan, Alberta, Northwest Territories), peatlands (Alberta), or silicate bedrock in the coastal range and islands of British Columbia. There are a few occurrences of acidification related to local influences.

Lake surveys conducted between 1977 and 1986 in Manitoba show that most of the waters of this province are well buffered from the effects of acidic precipitation (Table 4.1a.4). As in Ontario, the reason for this is the presence of carbonate bedrock or glacially dispersed carbonates in the surficial deposits (particularly in northeastern Manitoba; Kaszycki and DiLabio 1986). Only 13% of the lakes have $ANC < 200$ $\mu eq.L^{-1}$ while 31% have $Ca^{2+} < 200$ $\mu eq.L^{-1}$. The more sensitive lakes are found in the north western section of Manitoba between 55° to 58° N latitude and 100° to 102° W longitude (Lechner and Howard, 1987). This is the boundary area between Manitoba and Saskatchewan where Brochet, Lynn Lake, Sherridon and Flin Flon are located. A few lakes in this specific area have $pH < 5$ and are receiving mine drainage. Otherwise, only 0.1% of the entire Manitoba database has $pH < 5$. Waters having ANC in the range 200-400 $\mu eq.L^{-1}$ are found along the Manitoba-Ontario borders, in the general area of the Whiteshell and Nopiming Provincial Park. The remainder of Manitoba has waters with $ANC > 400$ $\mu eq.L^{-1}$; however, there is little information for the area north of 58°N latitude.

Approximately 0.5% of Saskatchewan's lakes have been sampled. There is a significant north-south variability in ANC, Ca^{2+}, and pH. ANC varies from 10-80,000 $\mu eq.L^{-1}$ and pH from 5.1-9.5. Less than 0.5% of the lakes have $pH < 6$ and these are located on the Precambrian Shield in the northern part of the province. They generally have $ANC < 200$

$\mu eq.L^{-1}$ although there are some instances of very dilute, sensitive waters; for example, 5 lakes located in the Cree Lake area of north-central Saskatchewan have specific conductivities of approximately 10 μS and ANC = 39-124 $\mu eq.L^{-1}$. Most other lakes in the province are less sensitive. The Shield contains about 89% (83,000) of the total number of lakes in Saskatchewan (Lechner and Howard, 1987).

Lake surveys in Alberta show that widely diverse areas of the province contain lakes with ANC < 200 $\mu eq.L^{-1}$ (approximately 3% of all those sampled). Many of these lakes are found on the Canadian Shield in the extreme northeastern corner of province; however, others are found in the Rocky Mountain National Parks region (most notably Jasper National Park) and on peatlands in the northern uplands regions (Caribou and Birch Mountain Uplands, and Clear Hills and Swan Hills Uplands). Lakes in these peatlands are highly coloured, muskeg-type lakes, typically having pH < 6.5. Only 1% of Alberta's lakes have a pH < 6.

Table 4.1a.4 Distribution of lakewaters from Manitoba, Saskatchewan, Alberta, and British Columbia within classes for pH, and Ca^{2+} and ANC ($\mu eq.L^{-1}$).

		Percent of sampled lakes			
	Class	Manitoba	Saskatchewan	Alberta	British Columbia
pH	<5.0	0	0	1	0
	5.0-5.9	1	0	1	1
	6.0-6.9	22	31	15	23
	>7.0	78	69	83	77
Ca^{2+}	<200	31	52	8	15
	200-400	24	12	9	17
	>400	45	36	83	66
ANC	<200	13	31	3	13
	200-400	33	13	5	18
	>400	55	56	92	69

In British Columbia, information has been obtained for 3.6% of the province's lakes; 13% of them have ANC < 200 $\mu eq.L^{-1}$. Most of the lakes are located within about 250 km ofthe marine coastline, on Vancouver Island or the Queen Charlotte Islands, and at several other scattered smaller areas near Atlin Lake, north from Stuart and Shuswap Lakes. Only about 1% of the lakes have pH < 6.

Depending on chemical parameter, information exists for 420-571 locations in the Northwest Territories (Tibbatts et al 1987) although it should be noted that many stations occur in clusters so that this very large area is only sparsely represented. Aquatic sensitivity reflects the major patterns expected from bedrock geology maps with a clear east-west division following the margin of the Canadian Shield (i.e. a north-south line between Great Bear and Great Slave Lakes). On the sensitive areas of the Shield to the east, all lakes exhibit pH<7.5, whereas to the west, lakes have pH>7.5 with only a few exceptions. For 22 lakes in the District of Keewatin, Edwards et al (1987) reported pH in the range 5.9-7.3.

4.1a.5 WETLANDS/PEATLANDS

Summary: While several effects of acidic deposition on wetland ecosystems are known, the most important response is storage of atmospherically deposited S and N for time periods of years to decades. This storage delays acidification of exported waters beyond that associated with the normal export of natural organic acids; however, most of the S and approximately half of the N stored in the surface layers of the peat are exported eventually accompanying oxidation of organic matter.

A "wetland" is land saturated with water long enough to induce aquatic processes; typically it will have poorly drained soils, hydrophytic vegetation and various kinds of biological activity adapted to a wet environment. Wetlands may be categorized into organic wetlands (peatlands) which have more than 40 cm of peat accumulation, and mineral wetlands which are influenced by excess water but have little or no peat (instead Gleysolic or peaty phase Gleysolic soils are produced, National Wetlands Working Group 1988). In the following discussion, "wetland" will refer specifically to organic wetlands since the available information on effects is restricted almost entirely to this type. Wetlands in Canada occupy 1.27 million km^2 (approximately 14% of the total land surface area; National Wetlands Working Group 1988). The distribution of wetlands by province is given in Table 4.1a.5.

Effects of acidic deposition on wetlands and wetland waters have been documented or hypothesized based on a knowledge of processes. They include: direct acidification (Gorham et al 1985; Gorham and Detenbeck 1986), increased export of mineral and organic acids (Gorham et al 1985; Urban et al 1987), mobilization of metals to toxic levels (Urban et al 1987; Helmer 1987), loss of plant and animal species (Tallis 1964; Gorham et al 1984), increased emissions of N and S gases (Hemond 1980; Bowden 1986; Urban et al 1989; Urban and Eisenreich 1988; Spratt et al 1987; Nriagu 1987), decreased enzyme activities in plants and peat (Woodin et al 1985; Lee et al 1987; Press et al 1985), and changes in carbon storage (Clymo 1987). Interpretation of anthropogenically induced acidification of wetlands is complicated by the existence of natural acidification processes and cation exchange (Wright 1983; Rogalla et al 1986); the relative effects are summarized by Wood (1989).

Current understanding of the effects of acidic deposition on wetlands has been derived

Table 4.1a.5 Extent and distribution of wetlands in Canada.

	Total Area ($km^2.10^5$)	% Total Area
British Columbia	0.31	3
Alberta	1.37	21
Saskatchewan	0.97	17
Manitoba	2.25	41
Ontario	2.92	33
Québec	1.22	9
New Brunswick	0.05	8
Nova Scotia	0.02	3
Prince Edward Island	0.00	<1
Newfoundland-Labrador	0.68	18
Yukon	0.15	3
Northwest Territories	2.78	9
CANADA	12.72	14

primarily from measurement of the acidity budgets for 3 wetlands in North America. The budgets show that acidity in wetland waters originates primarily from organic acids generated by incomplete oxidation of organic matter (Urban et al 1989). Estimated export of organic acidity from bogs in eastern North America is 100-250 $meq.m^{-2}.yr^{-1}$ (Gorham et al 1986; Urban and Bayley 1986). Lesser sources of acidity include biological uptake of cations and/or cation exchange, and anthropogenic H_2SO_4 and HNO_3 inputs (Urban et al 1987). Major exports of mineral acids occur only in wetlands which have been very severely impacted by acid deposition for long periods of time (Gorham et al 1985). Three features distinguish acidity budgets of wetlands from other ecosystems: high production and export of DOC, high storage of cations, and high anion retention (Urban and Bayley 1986). Acidic deposition affects primarily anion retention, and to a lesser extent, cation storage.

Wetlands neutralize acidic deposition by rapid uptake and storage of N (see discussion in Section 4.1a.7) and, to a lesser extent S. For example, at Thoreau's bog in Massachusetts, the annual retention of total S was 77%, while at the Experimental Lakes Area (ELA) in northwestern Ontario and Marcell in northwestern Minnesota, annual S storage was much lower at 38% and 37% respectively (Urban et al 1989). Retention of S by wetlands is maximized when hydrologic conditions favour increased contact between the water and the vegetation and peat (Wood, 1989). Most of the S input to wetlands is converted to organic forms within 2-3 months of deposition (Bayley et al 1988), and thus, organic S forms the largest component of the total S in wetland peats, generally >90% (Urban et al 1989).

4.1a.6 GROUND WATER STATUS

Summary: The chemical composition of ground water is regulated by the degree of mineral-water interaction which is in turn primarily regulated by the contact time. At the few sites where intensive ground water studies have been conducted, 2 ground water regimes often exist. Interaction is minimal in a near-surface (unsaturated) regime; here, ground water composition is more strongly influenced by precipitation chemistry and may experience episodic pH depressions during periods of high water flux. Deeper (saturated) ground water regimes show little evidence of acidification although this may not remain the case if acidic deposition continues in the long term. The generally high ANC of the ground water contribution to surface runoff acts to ameliorate the effect of acidic deposition, e.g. by minimizing the magnitude of episodic pH depressions.

Ground water sources make up a significant proportion of all water used in Canada, and in many locations, ground water is the primary source of supply. Twenty-six percent of Canadians use ground water for their domestic supply, and approximately 38% of municipalities rely entirely or partially on ground water (Hess, 1986).

The solutes present in ground water arise primarily from ion exchange and mineral dissolution reactions. Factors controlling these reactions include: chemistry of incident precipitation; depth, geochemistry and texture of unconsolidated materials overlaying the bedrock; bedrock characteristics; and in particular, the contact time of water with subsurface materials. The contact time regulates the degree to which exchange/dissolution reactions approach equilibrium conditions and this is controlled typically by the flow pathways taken by ground water prior to its re-emergence at the surface.

Most Canadian acidification-related ground water research has focused on defining water-mineral and ground water-surface water interactions. In the Turkey Lakes Watershed (Algoma, Ontario), the ground water flow system consists of 2 regimes (Craig and Johnston 1988a): rapid flow through a surficial, highly permeable zone (ablation till containing a very small quantity of $CaCO_3$), and slow flow in a deeper, less permeable zone (basal till with higher $CaCO_3$). In the shallow regime, ground water is classified as Ca^{2+}-SO_4^{2-} water reflecting the incomplete mineral-precipitation interaction that occurs in this zone. Also, high variability present in overburden characteristics leads to high spatial variability in ground water chemistry within the shallow regime. In the deeper zone, extended water-mineral interaction controls the ground water composition (i.e. they are Ca^{2+}-HCO_3^- waters) and yields more spatially uniform concentrations.

In the shallow ground water regime, short term acidification (ANC≤0) occur in response to large acid loading events such as spring melt (Craig and Johnston 1988b). Dissolution of the trace amount of $CaCO_3$ present in the overburden at Turkey Lake is insufficient to offset increased acidity during these high loading events, i.e. the rate of acid input temporarily surpasses the rate of acid neutralization provided by water-mineral interaction. During these near surface pH depressions, increased concentrations of K^+ (Craig and Johnston 1988b) and Al (Foster and Nicolson 1986; Chew et al 1988; see also Jeffries

and Hendershot 1989) have been reported as well. If acidic deposition continues unabated, the frequency and duration of the near-surface pH depressions in the ground water may increase as the soils become further depleted in exchangeable bases and/or readily soluble minerals. The overall rate of ground water acidification is unknown; however, regions of Scandinavia that have a long history of acidic deposition exhibit chronic ground water acidification (Henriksen and Kirkhusmo 1982, Hultberg and Johansson 1981).

Ground water greatly influences the composition of surface water. A large proportion of water present in streams was ground water previously, even during periods of storm or snowmelt runoff (e.g. 30-90% in some Ontario catchments; Bottomley et al 1984, 1986). The generally higher ANC and cation concentrations in the ground water has an ameliorative effect, minimizing the surface water pH depressions that occur during such episodes. Ground water has been pumped and mixed with the surface water as a means of artificially neutralizing a section of acid stream in Pennsylvania (Fisher 1985).

At present it is not possible to extrapolate results from intensive catchment studies to predict the regional condition of Canadian ground waters. The water-mineral interactions that provide most subsurface buffering of input acidity remain too poorly understood, and the site-to-site variability is too large.

4.1a.7 NITROGEN

Summary: The role of N in surface and subsurface water acidification is more complex than that of S. Consideration of NO_3^- levels in Canadian lakes suggests that acidification by N deposition is of minor consequence at this time; however, some isolated occurrences of either chronically or episodically high concentrations imply that it may be of greater importance in the future, particulary since NO_3^- deposition has remained fairly constant (rather than decreasing like SO_4^{2-}) over the last decade.

4.1a.7.1 REASON FOR CONCERN

The role of nitrogen in surface and subsurface water acidification is more complex than that of sulphur because a) the principal inorganic nitrogen species in atmosphere deposition are more biologically active than SO_4^{2-}, the principal S species, and b) there are two major N species in deposition having different oxidation status (NO_3^- and NH_4^+) as opposed to one S species (SO_4^{2-}).

While SO_x emissions in eastern North America have declined in the past decade resulting in a decrease in SO_4^{2-} deposition (Hedin et al 1987, Dillon et al 1988b), NO_x emissions and resultant NO_3^- deposition have remained fairly constant. This has resulted in a gradual increase in the equivalent ratio of NO_3^- to SO_4^{2-} in much of eastern North America, with ratios reaching 0.7 in southern Ontario. Ammonium deposition has also remained constant over the past 10-15 years. These trends have led to concern that the relative importance of N-species to acidification of aquatic and terrestrial systems may or has

increased (Kelly et al 1989). This, in fact, appears to be the case in parts of western Europe (Henriksen and Brakke 1988).

4.1a.7.2 BIOGEOCHEMICAL PROCESSES

The N cycle and its relationship to acidification of aquatic and terrestrial systems is reviewed by Keeney (1973) and Reuss (1975). The contributions of both NO_3^- and NH_4^+ to long-term acidification are controlled by biological processes, which generate or consume ANC (Brewer and Goldman 1976, Grennfelt and Hultberg 1986). Only those reactions involving a net change in charge on the N species have any effect on the acid-base balance. In aquatic systems, NH_4^+ is generally the preferred source of N for algae (Syrett 1981); thus high NH_4^+ deposition rates can generate considerable acidity via NH_4^+ assimilation (Schindler et al 1985). In addition, nitrification (microbial conversion of NH_4^+ to NO_3^-) creates two equivalents of acid for each equivalent of NH_4^+ nitrified, again contributing to the acidification of aquatic systems. High NH_4^+ loadings in parts of Europe are considered to be the major cause of acidification of ecosystems (van Breemen et al 1982).

The effects of NO_3^- on aquatic systems are also complex. Uptake (biological assimilation) and reduction (denitrification) are both ANC-generating processes, so the acidification by HNO_3 will be balanced to the extent that the NO_3^- is consumed in the aquatic (or terrestrial) systems. As a further complication, microbiological processes such as denitrification and nitrification may be affected by acidification and high SO_4^{2-} concentrations. Thus, Rudd et al (1988) found that acidification of Lake 223 (ELA) to pH=5.4-5.7 resulted in the cessation of nitrification.

4.1a.7.3 EFFECTS ON WATER

The overall effects of the N species on surface/subsurface acidification can be assessed using mass balance studies (Dillon and Molot in press). Because of the interconversions between NO_3^- and NH_4^+, mass balances of both species must be considered simultaneously. Such studies show that NH_4^+ is more efficiently removed than NO_3^- in most Canadian catchments with NH_4^+ retention rarely less than 0.9 and often >0.95. On the other hand, NO_3^- retention was found to be highly variable, ranging from 0.37-0.99 with almost all values less than the corresponding NH_4^+ retention. A similar pattern was true in lakes, although there were a few cases where NO_3^- retention exceeded NH_4^+ retention. In almost all cases, lakes were less efficient than their catchments in retaining both NH_4^+ and NO_3^-.

Based on the above considerations, it can be seen that the net effect of the N species with respect to system acidification is equal to the ratio of NH_4^+ to NO_3^- consumption (in equivalent or molar units); that is, if this ratio is >1, there will be net acidification of the system as a result of N species deposition. In Ontario lakes, this ratio exceeded 1.0 in 8 of 34 lake-years (7 lakes included). In the remaining 26 lake-years, NO_3^- consumption exceeded NH_4^+ consumption giving net neutralization or generation of ANC. This ratio

was strongly negatively correlated with $\bar{z}/\tau_w$ (lake mean depth/water replenishment time), and values >1 were much more likely to occur in lakes with long residence times. Net N consumption-based acidification of catchments also occurred in a number of Canadian sites; this phenomenon has been observed in parts of eastern USA as well.

In some regions in which surface waters are affected by acid deposition, ANC and pH reductions during spring snowmelt are believed to be of major biological significance (Jeffries et al 1979, Henriksen and Wright 1977, Keller 1983). These episodic acidification events are caused by base cation dilution and/or acid anion increases (Galloway et al 1980, Galloway and Dillon 1983, LaZerte and Dillon 1984, Molot et al 1989). Acid anions (SO_4^{2-} and NO_3^-) may dominate ANC depressions in areas of high deposition because anions accumulated in the winter snowpack (or in the case of NO_3^-, in near surface soils due to over-winter nitrification) are released in a relatively brief melt period (Johannessen et al 1977, English et al 1986). This typically occurs when biological activity in soils and streams is low; thus, ANC-producing redox reactions are insignificant within the period of spring melt. Since the NO_3^- - SO_4^{2-} ratio in deposition is highest in winter, the possibility of major N-species contribution to episodic acidification exists. However, an examination of changes in streamwater chemistry in 12 headwater streams and 3 lake outflows in Ontario for 3 years (Molot et al 1989), demonstrated that NO_3^- was not a significant contributor to pH/ANC depressions. NO_3^- typically contributed to depressions very early in snowmelt episodes, but the effects were very small in almost all cases.

4.1a.7.4 EFFECTS ON WETLANDS

At the current and projected rates of NO_3^- deposition in eastern North America (approximately 6-10 $kg.ha^{-1}.yr^{-1}$), NO_3^- acts mainly as a fertilizer stimulating plant growth in wetlands (Urban et al 1988; Urban and Eisenreich 1988) although retention by denitrification to NO_2 and dissimilatory reduction to NH_4^+ occurs also. Outputs of NO_3^- from wetlands are generally <5% of NO_3^- inputs (Hemond 1980; Urban and Bayley 1986; Urban and Eisenreich 1988). Output of total N may be higher. The rapid uptake by plants, however, does not preclude the possibility of N deposition contributing to acidification of surface waters since the long-term capacity for wetland uptake of N is limited. For example, increased NO_3^- export was observed only after 5 years of artificial acidification of a wetland at ELA (Bayley et al 1988); although large amounts of NO_3^- are still retained at ELA, the wetland is no longer protecting the downstream waters from acidification. Moreover, Urban and Eisenreich (1988) found that long term storage of N in deep peats is only 50% of the inputs at the surface layer.

Recent evidence from the ELA study indicates that bogs and fens respond differently to inputs of S and N. Both the oligotrophic (bog) part of the wetland, as well as the minerotrophic (fen) area received identical inputs of 50% HNO_3 and 50% H_2SO_4. The concentration of SO_4^{2-} in the oligotrophic part of the wetland increased shortly after the acidification experiment began while NO_3^- levels remained the same (Bayley et al 1988). In contrast, the minerotrophic (fen) area of the wetland exhibited unchanged SO_4^{2-} while surface water NO_3^- levels increased. The greater storage capacity of the bog for N than S probably relates to the greater affinity of Bryophytes than vascular plants for N (Press

et al 1985; Woodin et al 1985).

4.1a.8 EPISODIC AND SEASONAL ACIDIFICATION

Summary: Storage of acidity and associated mobile anions within the snowpack and/or the over-winter production of acidity in upper soil horizons can lead to the release of exceptionally high concentrations during early melt stages that may cause short term acidification of surface waters (i.e. pH depressions of 1 unit or greater). Change in water flowpaths during periods of high runoff is also an important factor governing the occurrence and magnitude of episodes. Both simple dilution as well as acidity and mobile anions from the snowpack or rain are involved in producing episodes.

Catchment mass budget analyses show that storage of SO_4^{2-} and/or oxidation of stored reduced sulphur may occur during dry seasons when hydrological fluxes are at a minimum. A SO_4^{2-} pulse in the outflow waters, perhaps with an associated acidification episode, accompanies initiation of the next wet season. The presence of wetlands is an important factor.

4.1a.8.1 EPISODES

Discussion above has focused on chronic acidification of waters; however, temporally limited periods of acidification may produce conditions that are detrimental to aquatic biota. For example, numerous episodic fish kills have occurred in Scandanavia (e.g. Leivestad and Muniz 1976; Henriksen et al 1984; see also review by Rosseland et al 1986); however, reports for Canadian waters are more limited (e.g. Harvey and Lee 1982; Harvey and Whelpdale 1986). When physical conditions permit, it is likely that biota possessing sufficient mobility simply evade the toxic waters thereby, reducing the overall effect.

Episodic acidification is associated with periods of high runoff, and since the major hydrological event in Canada each year is associated usually with spring snowmelt, Canadian research on episodes has focused on this time period. However, rainfall induced episodes have been reported also (e.g. Scheider et al 1979, Whitfield and Daley 1987).

Storage of ions (including acidity) within the snowpack and release of exceptionally high concentrations during early melt stages is a well documented phenomenon (reviewed by Jeffries 1990; Jones and Orville-Thomas 1987), and the effects (including biological effects) have been reviewed by Marmorek et al (1984). When flow rates and hydrological flowpaths change during periods of high runoff, water-soil interaction may be minimized and less neutralization of the acidity occurs. Hydrological literature on flowpath alteration is extensive, see brief review by Jeffries and Hendershot (1989). Both overland flow and subsurface quick-flow minimize water-soil interaction. Utilization of near-surface, acidic soil horizons for lateral flow (rather than deeper, less acidic horizons) yield runoff waters

with lower pH, ANC, base cation and sometimes A^- concentrations and often higher NO_3^- and Al concentrations than those observed during low flow conditions. When the snowmelt waters percolate through acidic soils, the high concentration of a mobile anion such as SO_4^{2-} carries acidity with it, thereby producing a pH depression. Combination of these hydrological and mobile anion factors governs the occurrence and magnitude of acidification episodes.

During snowmelt, surface water pH decreases on the order of 1 pH unit (occasionally much greater) have been observed in Ontario (Jeffries et al 1979; Jeffries and Semkin 1983; Gunn and Keller 1984; LaZerte and Dillon 1984; Kelso et al 1986), in Québec (Jones 1987), and the Atlantic provinces (Clair and Freedman 1986; Kerekes et al 1986; Freedman and Clair 1987). The pH depressions are related to both simple dilution of baseflow ANC and C_b* (Galloway et al 1987; Semkin and Jeffries 1988) and flowpath alteration as noted above. Using isotopic fractionation, Caron (1984) demonstrated that most of the SO_4^{2-} in surface waters is of atmospheric origin. This conclusion appears also true for the springmelt period as shown by chemical budgets for Lac Laflamme (southern Québec) presented by Jones and Bedard (1987). Elevated NO_3^- that sometimes accompanies the pH depressions may originate from the pulse released from the snowpack during early melt or from a washout of NO_3^- produced by over-winter nitrification within near surface soils. Jones and Bedard (1987) have shown that atmospheric deposition can account for nearly all the NO_3^- present in Lac Laflamme runoff waters during snowmelt. However, contemporaneous peaks in NO_3^- and Al concentrations such as those observed at Hubbard Brook, New Hampshire (Driscoll et al 1985) lend support to the second hypothesis as well, although desorption of Al from the stream bottom substrate during pH depressions has been observed also (Norton et al 1987). Further discussion on the role of NO_3^- during snowmelt episodes is given in Section 4.1a.7.3. Finally, LaZerte and Dillon (1984) and Clair and Freedman (1986) have shown that springmelt pH depressions are more related to variations in anthropogenic strong acids than in naturally occurring organic acids.

The chemical effect of snowmelt on lakes is governed by the physical process controlling meltwater dispersion under the ice (e.g. drainage basin characteristics, lake morphology and residence time, climate). The cold and therefore less dense incoming meltwaters spread out across the lake in a layer 1-3 m thick (Gunn and Keller 1985; Bergmann and Welch 1985; Jeffries and Semkin 1983) and its chemical composition is very similar to that observed in streams, e.g. reduced pH, ANC, C_b* (Jeffries and Semkin 1983; Charette et al 1984) and elevated NO_3^- and Al (Hasselrot et al 1987; Jeffries and Hendershot in press). While low ANC concentrations (depression from 140 to near 0 $\mu eq.L^{-1}$) in Lac Laflamme have required several months to recover to pre-melt levels (Charette et al 1984), in many other lakes, incoming acidic meltwater may in fact exit the lake via the outflow thereby minimizing its effect on lake-dwelling biota. However, biological habitat such as lake trout spawning beds (Gunn and Keller 1984) may be directly affected by the acidic layer, and in very small lakes and streams where nearly the entire water mass is replaced by more acidic meltwaters, more extensive biological effects may occur. Studies at Lac Laflamme (Charette, pers. comm.) have shown that acidity levels in near-shore waters can be much higher than at the lake centre; in the absence of rainfall, high values often coincide with the first 20-30% of the snowmelt.

4.1a.8.2 SEASONAL ACIDIFICATION

Catchment mass budget analyses show that storage of SO_4^{2-} and/or oxidation of stored reduced S may occur during dry seasons when hydrological fluxes are at a minimum; a SO_4^{2-} pulse in the outflow waters accompanies initiation of the next wet season. For example, Kejimkujik watersheds in southwestern Nova Scotia exhibit strong seasonal patterns in SO_4^{2-} concentration that are inversely related to discharge and DOC (Kerekes et al 1986); while natural organic acids reduce the average pH of Kejimkujik waters, anthropogenic SO_4^{2-} is the primary factor influencing shorter term variations in acidity.

The presence of wetlands is an important factor. Sulphate pulses have been observed in many wetlands in North America (Brown 1980; Rippon et al 1980; Brakke 1981; Weider and Lang 1982; Behr 1985; LaZerte and Dillon 1985; Weider et al 1985; Bayley et al 1987). At ELA, SO_4^{2-} in runoff waters increased 40-fold above summer levels following the first rainfall event in September (Bayley et al 1987) although Ca^{2+} and Mg^{2+} were the counter ions rather than H^+. At other locations, a significant H^+ pulse accompanies the SO_4^{2-} pulse (e.g. Dorset, Ontario, LaZerte and Dillon 1985; Storgama, Norway, Brakke 1981). The nature of the SO_4^{2-} pulse is related to the base saturation of the wetland (Bayley et al 1987); that is, coincident SO_4^{2-} and H^+ pulses occur in wetlands that have been exhausted of base cations (ombrotrophic or oligotrophic systems) or other wetlands that have received high deposition for an extended period.

4.1a.9 TRENDS IN AQUATIC CHEMISTRY

Summary: Algal microfossils buried in sediments have been used to infer historical changes in lake pH. Nine of the 36 lakes studied have experienced recent (i.e. last 100-150 years) pH declines that are attributed to acidic deposition. The lakes occur in all regions of eastern Canada. Studies have also documented both pH declines during the past 50-100 years caused by nearby smelter emissions, and recent pH increases resulting from application of emission controls.

Reliable chemical records approximately a decade long now exist for a few acid sensitive eastern Canadian lakes and streams. This monitoring shows that different ecosystems respond differently. Some waters such as those near Sudbury and in Algoma, Ontario appear to be very responsive exhibiting changes in water chemistry during the 1980s that reflect changes in acidic deposition. Some lakes in Québec and the Atlantic provinces similarly exhibit trends consistent with changes in deposition; however, there are lakes in all eastern Canadian provinces that show no trends, or in a few cases, trend opposite to that expected. Such responses are probably related to terrain characteristics, e.g. storage and release of acids in the terrestrial watershed. Wetlands can play a key role in this regard.

4.1a.9.1 PALEOLIMNOLOGY

When historical data on past water chemistry are not available for a lake, algal microfossils deposited in lake sediments generally can be used to date the onset and rate of lake acidification (Charles and Norton 1986; Smol et al 1986; Dixit et al 1987), or to monitor recovery of acidified lakes (Battarbee et al 1988; Dixit et al 1989). Many diatom and chrysophyte algal species have very specific pH requirements (Charles et al 1990) and determining the presence/absence of these species in sediment strata forms the basis of the technique. Metal profiles in sediment cores have been used also to make historical inferences.

Paleolimnological studies have been completed or are underway in almost every major geographic region of the world that is susceptible to acidification. In eastern Canada, sediment profiles have been examined from 37 lakes (1 experimentally acidified) in Ontario, Québec, Nova Scotia, New Brunswick, and Newfoundland (see reviews by Cook et al 1988, Dixit and Smol 1989, and particularly, Table 1 in Charles et al 1990). Both statistically significant and insignificant changes from the inferred historical lake pHs are reported. Twenty-two of 36 cases exhibited little difference between current lake pHs and historical values while the remaining 14 cases showed recent pH declines that could be related to either local mining/smelting influences or acidic deposition from long range sources (Charles et al 1990). This is as expected given the strong and variable control over ANC depletion exerted by terrain characteristics as discussed above. Some evidence of the effect of forest fire and/or logging was seen in a few locations as well. Overall, 9 of the 36 cases exhibited pH declines during the past 100-150 years that can be attributed to LRTAP (Charles et al 1990). They are found in all eastern Canadian provinces. Charles et al (1990) also note that the pH declines are generally proportional to S and N deposition. Comparable paleolimnological studies have found no evidence of pH declines in North American and European lakes that receive low deposition.

Many studies have been located near major point sources (e.g. smelters at Wawa and Sudbury, Ontario) in order to document historical decreases in lake pH and/or increases in heavy metal sedimentation that accompanied operation of the smelters. The paleolimnological records show that changes in lake chemistry occurred during the past 50-100 years, in general agreement with the known history of these sources. Also, Dixit et al (1989) have shown that inferences made using chrysophycean microfossils correspond well to the measured pH increases recorded during the last decade for a Sudbury area lake (see following Section).

4.1a.9.2 LONG-TERM MONITORING

Long term records of water chemistry (multiple decades) provide the only means for directly assessing past trends in water chemistry as they relate to the effect of acidic deposition. Probably the longest North American records useful in this context are from the Hubbard Brook Experimental Forest, New Hampshire (Likens et al 1977) which are now over 20 years in duration. Unfortunately, such long term records do not exist for sensitive lakes or streams in Canada although a few sites have been monitored

continuously over approximately the last decade, and some of them provide evidence of chemical trends. In terms of the reversibility of acidification of aquatic systems, Hauhs and Wright (1988) and Barth (1987) have provided reviews recently that include some Canadian information.

Sulphur dioxide emissions from the smelters at Sudbury declined from about 2.2×10^6 tonnes in 1950-72 to about 0.65×10^6 tonnes by 1979-85. In addition, the replacement of relatively short stacks (<200 m) with a tall stack (381 m) at the largest smelter in 1972 almost certainly resulted in dispersal of SO_2 over a much greater area. Consequently, S deposition decreased locally, perhaps by as much as 75% (Dillon et al 1982; Hutchinson and Havas 1986). Several lakes in the immediate vicinity of Sudbury were studied extensively over this time period (Dillon et al 1979, 1982, 1986; Dillon 1984; Yan and Dillon 1984; Hutchinson and Havas 1986), all of them exhibiting substantial decreases in lake water SO_4^{2-} (25-65% to 1984) and increases in pH and ANC (see Figure 4.1a.10 and Table 4.1a.6). Where metals were measured, decreases in Al, Cu, Ni, and Zn were observed also. Lakes that were not manipulated with $CaCO_3$ or $Ca(OH)_2$ showed

Table 4.1a.6 Percent change in the concentrations of SO_4^{2-}, H^+, and ANC for lakes near Sudbury after reduction in local SO_2 emissions. Pre-reduction concentrations ($\mu eq.L^{-1}$) are shown brackets.

Lake	SO_4^{2-}	H^+	ANC[1]
Clearwater[2]	-32 (545)	-59 (59)	+47 (-59)
Middle[2,4]	-34 (850)		
Hannah[2,4]	-44 (1150)		
Lohi[2]	-25 (525)		
Swan[2]	-62 (580)	-85 (110)	+285 (-66)
Baby[3]	-58 (1500)	-98 (79)	
Alice[3]	-65 (5540)	-80 (0.8)	

1 ANC is calculated by ion balance ignoring NO_3^- and Cl^-
2 From Dillon et al (1986)
3 From Hutchinson and Havas (1986)
4 Treated with $CaCO_3$ and/or $Ca(OH)_2$

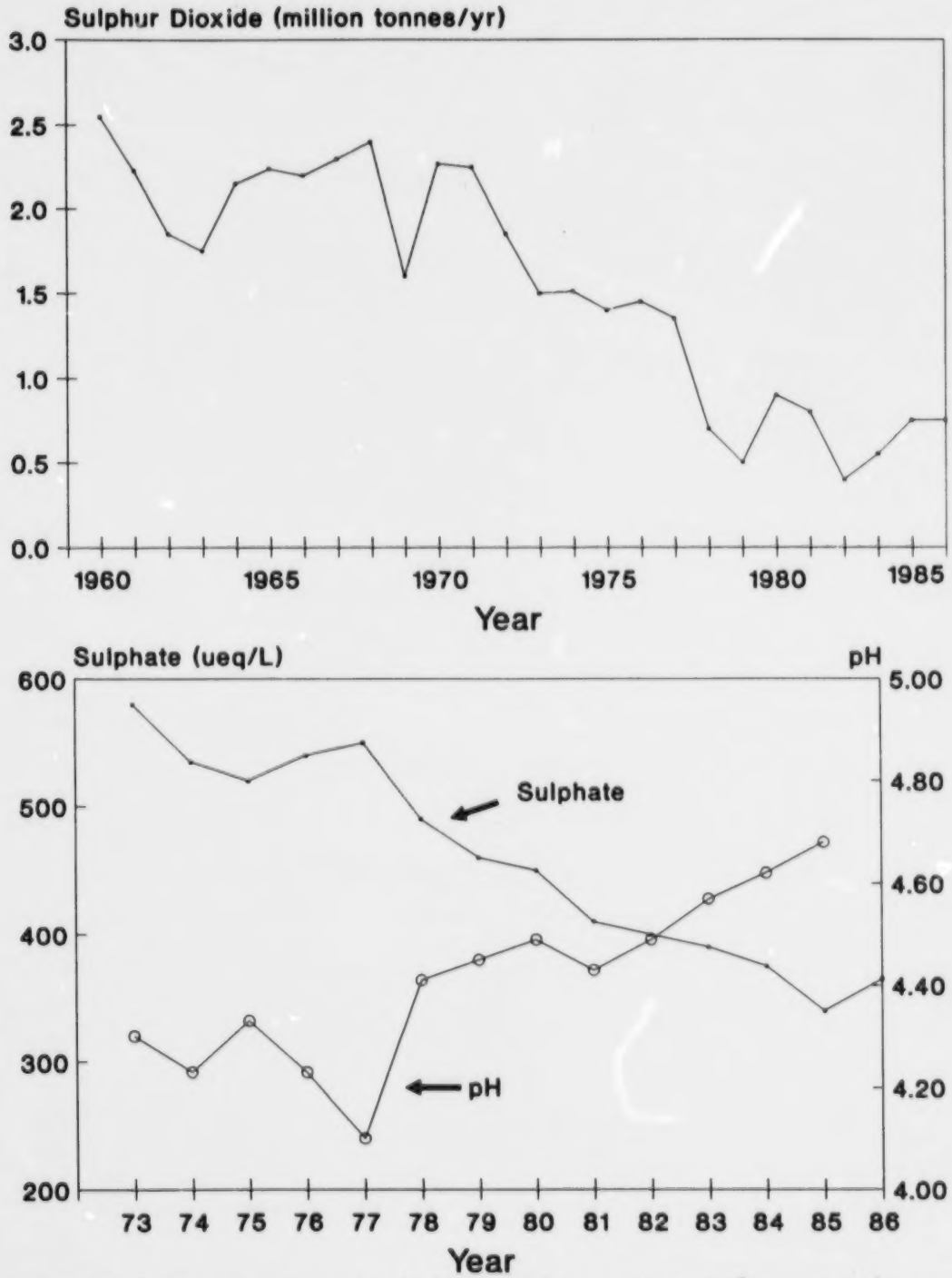


Figure 4.1a.10: Temporal variation in (a) the SO_2 emissions (10^6 tonnes.yr^{-1}) from the Sudbury basin (1960-85), and (b) pH and SO_4^{2-} in Clearwater Lake (1973-86) (after Dillon et al 1986).

declines in C_b* that were smaller than declines in strong acid anions. Since 1986 (i.e. beyond the period shown in Figure 4.1a.10), the SO_4^{2-} and pH trends in Sudbury area lakes have stabilized, showing neither increases or decreases (P.J. Dillon, pers. comm.).

These changes were evident also in lakes throughout the Sudbury region that were outside the immediate influence of the smelters (Keller et al 1986; Keller and Pitblado 1986). Comparison of the chemistry of lakes surveyed in 1974-76 and again in 1981-83 demonstrated that a decline in SO_4^{2-} and increase in pH occurred. Clearly, the decrease in SO_2 emissions at Sudbury has resulted in a rapid reversal of chemical acidification. On the other hand, evidence for the reversal of biological effects is less extensive. Salmonid populations in a few lakes relatively remote from the smelters have responded positively (Gunn and Keller 1984; Gunn et al 1988) to an increase in pH from 5.0 to 5.8. Limited information on the rotifer community (MacIsaac et al 1986) in 1 lake suggests improvement, but in general, information is scarce, and possibly confounded by the presence of relatively high levels of trace metals in many Sudbury lakes.

The Algoma area of central Ontario lies west of and outside the direct influence of the Sudbury smelters. A chemical survey of 54 lakes on a 3-year time step beginning in 1979 has shown that lakes in Algoma respond rapidly to changes in reduced SO_4^{2-} deposition with either increased pH and ANC or decreased C_b* (Kelso and Jeffries 1988). Two lakes without fish in 1979 and pH<5.5 developed white sucker (Catostomus commersoni) populations by 1986 with ages indicating that survival began after 1980, probably due to invasion from downstream populations when pH approached 5.5.

Of the 2 lakes in south-central Ontario (AG 17) that have been studied in-depth over the last 10 years (Dillon et al 1987), one (Harp Lake) is relatively insensitive to acidic deposition because of the thick glacial overburden present in its catchment. The other, Plastic Lake, has very thin overburden typical of sensitive systems. ANC decreased in Plastic Lake between 1979 and 1985 by about 2 $\mu eq.L^{-1}.yr^{-1}$ while that in Harp Lake did not change (Figure 4.1a.11). Contemporaneous to the ANC decrease in Plastic Lake, there was a pH and base cation decline, but no significant change in SO_4^{2-}. DOC also decreased and water transparency increased as the lake became more acidic. These chemical changes coincided with major biological changes in Plastic Lake although the pH decrease was only 0.2 units (from 5.8 to 5.6) over this time period (Dillon et al 1987). This measured decline in ANC for Plastic Lake likely represents only the "tail -end" of its acidification. Using the MAGIC model (Cosby et al 1985) combined with current lake and soil chemistry, and estimated historic precipitation chemistry, pre-industrial (ca. 1840) lake ANC was estimated to be 80-100 $\mu eq.L^{-1}$ (P.J. Dillon, unpublished studies). Thus, 75-80% of the original ANC of Plastic Lake may have been lost before studies began in 1979.

In the past few years (1986-88), the pH and ANC of Plastic Lake have remained constant despite a sharp decrease in SO_4^{2-} and H^+ deposition in southern Ontario in the past decade (Dillon et al 1988b). This is explained by continuing release of SO_4^{2-} and acidity from lowland (wetland) areas in the catchment despite decreasing SO_4^{2-} and increasing pH and ANC in waters draining upland portions of the catchment (P.J. Dillon, pers. comm.). It is hypothesized that the wetlands act as reservoirs for the mobile anion, and will continue to supply strong acid for an extended period of time following reductions of

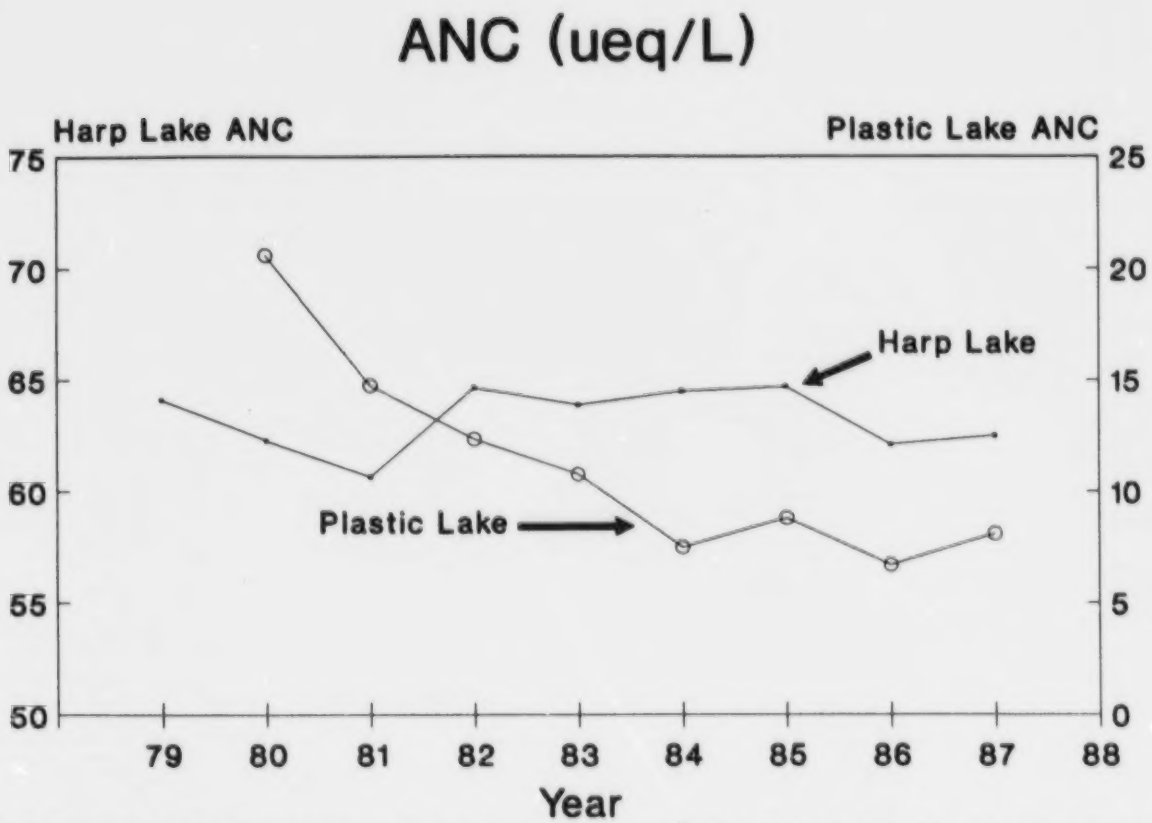


Figure 4.1a.11: Temporal variation in ANC ($\mu eq.L^{-1}$) in Harp and Plastic Lakes (south-central Ontario) from 1979 to 1987.

acidic deposition.

In Québec, temporal changes in water chemistry have been evaluated within the chemical budget studies conducted at Lac Laflamme in AG 14 (Papineau 1987), and a network of 64 lakes in AG 13, 14, and 15 that was specifically designed to detect statistically significant trends (Haemmerli 1988). Non-parametric tests applied to the network data covering 1983-88 give differing results depending on region. In AG 15, there was a statistically significant decrease in SO_4^{2-} of about 20 $\mu eq.L^{-1}$ over the 5 year period, consistent with changes in precipitation chemistry; however, no trend in pH or ANC has been detected yet.

In Ag 14, SO_4^{2-} increased during the first 3 years (accompanied by decreases in pH), but then decreased to level off at higher concentrations than those measured initially; hence only 2 network lakes (Lemaine and Laflamme) in this area had statistically significant trends over the 5 year period. Once again, these changes reflect variation in SO_4^{2-}

deposition. Two network lakes (Bonneville and Lagou) in the eastern portion of Ag 14 that have low ANC ($<20\ \mu eq.L^{-1}$) and whose pHs have not recovered since reductions in deposition, have exhibited statistically significant decreases in pH. There is also paleolimnological evidence of acidification for both lakes (Dixit et al 1987). At Lac Laflamme, decreases in atmospheric deposition (SO_4^{2-}, NO_3^-, H^+) after 1985 were accompanied by decreasing trends in lake water SO_4^{2-}, H^+, NO_3, Ca^{2+}, and an increase in colour.

In Nova Scotia, there are several rivers in which Atlantic salmon are either threatened with extinction or are known to have disappeared; several studies have attempted to determine chemical trends in them. Clair and Whitfield (1983) were able to apply a time series analysis to 8 Nova Scotian rivers located on "sensitive" terrain and determined that during the late 1960s and early 1970s, 5 of them exhibited a decreasing pH trend (the other 3 showed no trend). Thompson (1986) assessed changes in the chemical status of 11 rivers by comparing data collected in the early 1970s with data from the early 1980s. Taking into consideration changing analytical methodologies used to measure SO_4^{2-}, Thompson showed that mean annual SO_4^{2-} levels were lower in the latter period (all eleven cases) and pH was generally higher (9 of 11 cases). These findings corroborated earlier conclusions that 3 rivers experienced pH declines from the mid-1950s to the mid-1970s followed by a pH increase (Thompson et al 1980). Finally, during the 1980s, Watt et al (1990) monitored 9 rivers on a monthly basis; data for 1980-86 show declining pHs in 4 of 9 rivers; however after 1986, pHs improved so that when examined for the period 1980-88, only one river showed an overall pH decline.

Overall, monitoring of lakes and rivers in eastern Canada demonstrates that many of them chemically respond rather rapidly to changes in deposition. Lakes having wetlands within their drainage basins may not respond as quickly due to the temporary storage and release of acidic anions. Much less is known about the rate of biological responses; they are undoubtably much slower than the chemical changes although areas exhibiting improvements in water quality provide some positive signs (see also Section 4.1b).

4.1b WHAT EVIDENCE EXISTS DEMONSTRATING BIOLOGICAL DAMAGE TO AQUATIC ORGANISMS DUE TO DIRECT OR INDIRECT EFFECTS OF TOXIC SUBSTANCES ASSOCIATED WITH ACIDIFICATION OF AQUATIC ECOSYSTEMS?

Summary: Over the past 10 years our scientific understanding of the effects of acidic deposition has expanded greatly. There is now conclusive evidence that acidification of aquatic ecosystems causes adverse effects on many aquatic organisms. Direct effects of acidification to aquatic organisms are usually changes, frequently toxicity, caused by the chemical components in acid rain. Hydrogen ion is the primary toxicant, but its effects can be accentuated if low Ca^{2+} concentrations are present in the waters receiving the acidic deposition. Aluminum concentrations can increase in acidified waters and this can be toxic, also. Indirect effects of acidification are usually changes in organisms caused by interactions with other directly impacted organisms. The focus in this document will be on damage to fishes, but invertebrates (zooplankton, zoobenthos), plants (algae, phytobenthos), amphibians, and wetland birds are also discussed. The evidence comes primarily from three types of studies: bioassays, field surveys, and whole lake experiments. Bioassays provide some of the best evidence of direct effects of acidification. Survey and whole ecosystem experiments provide a mixture of direct and indirect effects.

In general, the total number of species present in fish, phytoplankton, zooplankton, and zoobenthos communities start to decrease at pH<6.0. There is an accelerating continuum of losses as pH declines further (Table 4.1b.1). Extensive algal mats develop along the shoreline of many lakes when pH<5.8, and an odiferous algae species sometimes appears at approximately the same pH. Some important sport fishes can be lost from lakes with pH<5.6, while species such as Atlantic salmon and brook trout are usually present until pH<5.1. An overall pH of 6.0 will ensure the continued presence of important Canadian sport fishes as well as other important components of aquatic ecosystems.

4.1b.1 FISHES

Summary: Many fish species are adversely affected by acidification. Extensive bioassays, field surveys, and experimental whole lake acidifications in Canada indicate damage often occurs when pH<6.0. Relative species sensitivities generally agree (e.g. fathead minnow > lake trout > white sucker) whether determined by bioassay, field survey, or whole lake experiment. Minnow species and other smaller fishes are frequently more sensitive than many sport fishes. Successful reproduction can occur in formerly non-reproducing populations by reversing acidification.

Table 4.1b.1 Examples of losses or appearances (denoted by *) of aquatic species in Canadian waters for 3 pH classes between pH 6.0 and 4.0. In general, fewer fish, algae, zooplankton, and zoobenthos species are present as pH decreases. Only common names are given; corresponding scientific names are present in the text.

	pH Range		
Taxa	6.0 - 5.6	5.5 - 5.1	5.0 - 4.0
Fishes	common shiner fathead minnow slimy sculpin blacknose shiner bluntnose minnow	lake trout white sucker walleye smallmouth bass lake whitefish	yellow perch brook trout Atlantic salmon
Algae	odiferous algae* shoreline algal mats*		
Zooplankton	water flea	2 copepod species	
Zoobenthos	3 crayfish species freshwater shrimp 1 snail species 7 mayfly species	1 amphipod species 5 leech species 3 mayfly species	4 mayfly species
Amphibians			many frog, toad, and salamander species
Wetland Birds	common loon	osprey ring-necked duck	tree swallow

4.1b.1.1 BIOASSAYS

The death of fishes exposed to acidified waters is well documented using laboratory or field bioassays (Haines 1981; Holtze and Hutchinson 1989; Kelso et al 1990). Differences in sensitivity of egg, sac fry, emergent fry, juveniles, and adults frequently occur as well as differences between species. Typically, younger life stages, especially newly hatched fry or fry feeding for the first time, are extremely sensitive. Some species, such as yellow perch (Perca flavescens) and brook trout (Salvelinus fontinalis), can tolerate very acidic exposures (pH < 5.0) while other species, such as rainbow trout (Oncorhynchus mykiss) and Atlantic salmon (Salmo salar), die during similar exposures. In a recent study, Holtze

and Hutchinson (1989) exposed eggs and fry of 6 species to Al and low pH and determined survival thresholds of (1) pH=5.9 for the minnow species common shiner (Notropis cornutus), (2) pH=5.4 for lake whitefish (Coregonus clupeaformis), white sucker (Catostomus commersoni), and walleye (Stizostedion vitreum vitreum), and (3) pH=5.1 for smallmouth bass (Micropterus dolomieui) and largemouth bass (Micropterus salmoides). Acid toxicity to Canadian fish species is usually eliminated during bioassay exposures when the pH is ≥6.0.

Because of the importance of Atlantic salmon in Canada, bioassays have been conducted on a wide variety of life stages of this species. In young salmon, acidification affects hatching success (Lacroix 1985b), emergence of fry, salmon parr (Lacroix 1985a; Lacroix and Townsend 1987; Lacroix et al 1985), and transformation of parr to smolt (Saunders et al 1983; Johnston et al 1984) . It also affects reproduction, hormone metabolism, growth, and survival in sexually maturing adults (Freeman et al 1983; Freeman and Sangalang 1985; Sangalang and Freeman 1987), as well as changes in gill histology and morphometry, and a wide variety of physiological parameters (Brown et al in press; Harvey et al in prep.; Majewski et al in prep.; Jagoe and Haines in prep.; Wesson et al in prep; Willis et al in prep.).

While results of bioassay experiments usually give concise, clear indications of low pH toxicity, relating the bioassay pH thresholds to effects in actual natural populations is frequently difficult. Kelso et al (1990) recently examined many laboratory studies and concluded that fishes in field situations were more sensitive than one would predict based on laboratory data. Holding organisms in containers also inhibits natural behaviours such as feeding and behavioral avoidance of low pH (e.g. Gunn and Noakes 1987; Peterson et al 1989). Refinements in techniques and exposures in more realistic conditions has narrowed the gap between apparent pH thresholds for toxicity in natural populations and pH thresholds in bioassays (Huckabee et al 1989; Holtze and Hutchinson 1989).

4.1b.1.2 FIELD SURVEYS

4.1b.1.2.1 Sudbury

Some of the earliest evidence in North America for fish population losses due to lake acidity are from lakes in the LaCloche Mountains near Sudbury, Ontario. Fish populations started to disappear from these seemingly pristine, clear lakes in the 1950s and 1960s (Harvey and Lee 1982). Researchers soon realized that the problem was lake acidification, and that Sudbury smelters were the likely source of toxicants (Beamish 1976). The disappearance of fish populations from these lakes is described in Beamish and Harvey (1972), Beamish (1974), Beamish et al (1975) and Harvey and Lee (1982). In addition to acidity, metal deposition (Cu, Ni, Zn) occurred in many lakes. Young fish were missing from many populations and some species appeared more sensitive than others. These survey results were similar to those of other field studies in areas of the world receiving significant acidic deposition (Haines 1981; Rosseland et al 1986).

Recently, pH has increased in many Sudbury lakes, due primarily to decreased emissions

from Sudbury smelters (Keller and Pitblado 1986; see section 4.1a.9.2). In Whitepine Lake, where a residual population of non-reproducing adult lake trout (Salvelinus namaycush) occurred, production of young trout started when lake pH rose above 5.5 (Beggs and Gunn 1986; Gunn and Keller in press). In Joe Lake, a reproducing brook trout population was established after water quality improved (Gunn et al 1988). In addition, lake pH has improved in more than 25 former lake trout lakes (Gunn and Keller in press), allowing fishery managers to stock hatchery reared lake trout and begin rehabilitation of sport fisheries in this area. Kelso and Jeffries (1988) report the reinvasion of white sucker between 1979 and 1986 in two Algoma district lakes, apparently occurring when lake pHs increased to levels near 5.5.

The combination of (1) fish population losses in lakes near Sudbury during high acidic deposition and low lake pH, and (2) recovery of populations during lower deposition and higher lake pH are strong evidence of the link between acidic deposition and stress on fish populations. The evidence of recovery also indicates that abatement of industrial emissions will not only protect sensitive aquatic systems, but that damaged systems can recover as productive resources.

4.1b.1.2.2 Ontario

The Ontario Ministry of Natural Resources has used extensive survey data to examine relationships between fish species presence/absence and water chemistry (Wales and Beggs 1986; Beggs and Gunn 1986; Matuszek and Beggs 1988; Matuszek et al in press, Matuszek and Wales 1990). Fish survey data were gathered on 9000 lakes and 3200 of these had recent chemical data (Green et al 1987). When effects of lake size were taken into account (large lakes usually have more fish species than smaller lakes), a decline in number of fish species occurred below pH = 6.0 (Matuszek and Beggs 1988; Matuszek et al in press; Figure 4.1b.1). Cyprinids (minnow species) were very sensitive to low pH and their abundance declined below pH = 6.0 (Matuszek et al in press). Four of the most acid-sensitive species of minnows were: common shiner, fathead minnow (Pimephales promelas), bluntnose minnow (Pimephales notatus), and blacknose shiner (Notropis heterolepis) (Matuszek et al in press).

Beggs and Gunn (1986) examined survey data for lakes that historically had supported populations of lake trout or brook trout. Lake trout were absent from lakes with pH < 5.2 and reproducing populations were restricted to lakes with pH > 5.5. No brook trout were found in lakes with pH < 5.0.

The total number of sport fish populations lost due to acidification was calculated using (1) observed pH thresholds for mortality of each species based on field survey data (pH = 5.5 for lake trout, walleye, and smallmouth bass; pH = 5.0 for brook trout), (2) atlases describing historical species distributions (Beggs et al 1985; OMNR 1987a, 1987b), and (3) the extensive Ontario chemical data set (Green et al 1987). The estimated number of lakes that have either lost their populations or had residual non-reproducing populations in Ontario (1981-1984) were 119 lake trout, 43 brook trout, 52 smallmouth bass, and 14 walleye populations (Table 4.1b.2; Matuszek and Wales 1990). The number of lost lake trout populations is particularly significant because there are few lake trout lakes; less

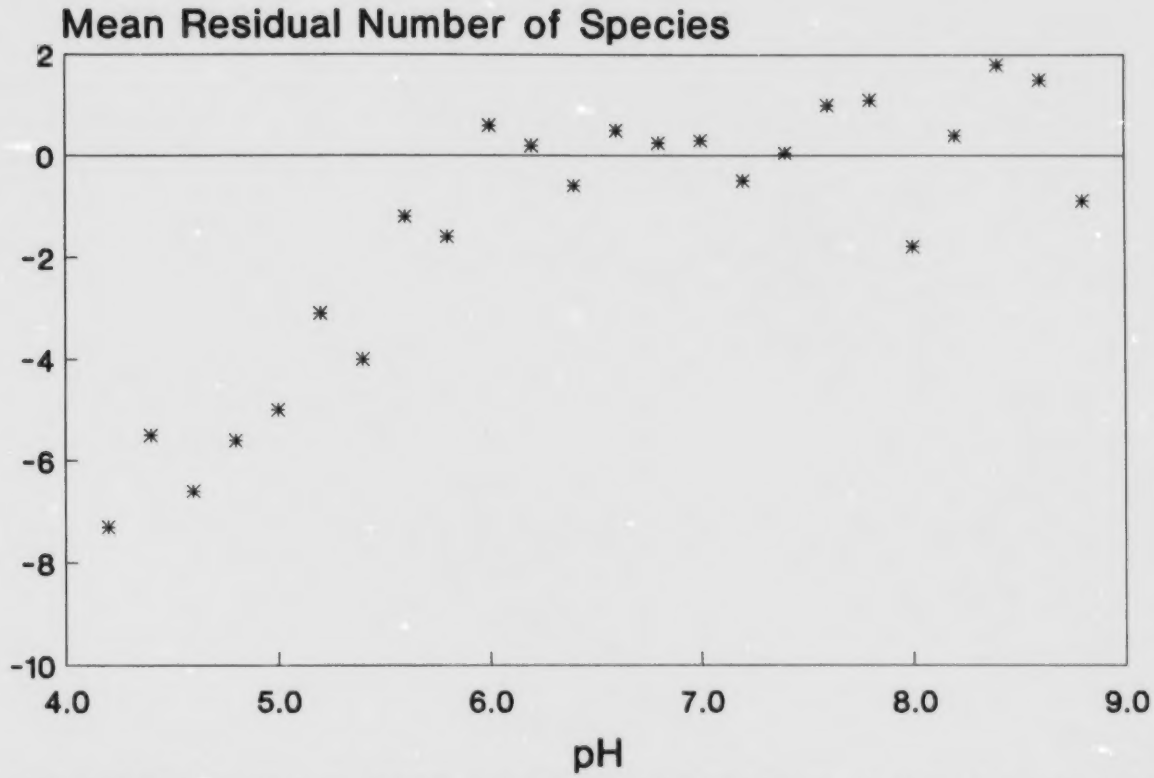


Figure 4.1b.1: Mean residual number of species (deviation of observed from that predicted by lake area) by pH in Ontario lakes (after Matuszek et al 1988).

than 1% of Ontario lakes contain this species (Martin and Olver 1976). Ontario also has considerable responsibility for this species, because approximately 20% of the world total of lake trout lakes are in its jurisdiction (Martin and Olver 1976).

Few data exist to construct the natural distributions of cyprinids and most other nonsport fish species in Ontario. Estimates for losses of these populations cannot be derived using techniques similar to those for sport species. However, the decline in species richness below pH=6.0 can be used in simulation models (see Section 4.3) to estimate acid related damage to the entire fish assemblage.

4.1b.1.2.3 Québec

Surveys conducted in the southern portion of the Canadian Shield region of Québec clearly indicated effects of lake acidity, low Ca^{2+}, and high Al on fishes (Langlois et al 1983; Frenette 1986; Richard 1985, 1986, 1988; Tremblay 1989; Tremblay and Richard in prep.). Lower total catches, lower catch rates, and smaller fish size of brook trout

Table 4.1b.2 Estimated number of acid affected populations of sportfish in Ontario Lakes (Matuszek and Wales 1990).

Number of Lakes	Species			
	Lake trout	Brook trout	Smallmouth bass	Walleye
Total in Ontario	2318	2100	2421	4038
Sampled	1296	639	901	989
Sampled with pH < species threshold	78	8	27	7
Estimated with pH < species threshold	119	43	52	14
Affected lakes in Sudbury Area	94	14	18	7

occurred in lakes with higher lake acidity (Richard 1985). In the Charlevoix area, brook trout abundance was negatively correlated with lake acidity (Richard 1986), and according to local fishermen, brook trout populations had disappeared from the three most acidic lakes (pH<5.1) between 1960 and 1980. Restocking these three lakes has failed.

In the Outaouais area, fish diversity was lower in lakes with lower pH (Tremblay and Richard in prep.). Diversity was lower in coloured lakes (>30 Hazen units) as well as in clearer lakes (<30 hazen units). Minnows were absent from lakes with pH<5.1. Acidic lakes had lower fish biomass than non-acidic lakes. Using the fish diversity relationship, the present pH lake frequency distribution, and the estimated pre-industrial lake pH frequency distribution (Dupont and Grimard 1989), Tremblay and Richard (in prep.) estimated that a minimum of 10,700 fish populations (23%) have disappeared from the Outaouais area since the onset of anthropogenic acidification.

The size frequency distribution of populations in the Outaouais and Northern Mauricie areas indicated recruitment failures were occurring for fishes in lakes with pH<5.5, but not in lakes with pH>5.5. Twenty-eight fish species were captured in these surveys; 80%

of the total number of species did not occur in lakes with pH=5.0-5.5. In the Mauricie area, fewer pearl dace (Semotilus margarita) and brook trout populations occurred in more acidic lakes, even when predaceous fishes such as walleye and northern pike (Esox lucius) were absent. These species were caught less frequently in lakes with higher dissolved Al concentrations (Tremblay 1989).

4.1b.1.2.4 Nova Scotia

One-third of the available Atlantic salmon habitat in Nova Scotia has been lost due to acidification since 1950. This is a loss to the salmon fisheries of about 9,000-14,000 fish per year and is almost equal to the current annual catch (Watt 1986). The southern uplands region of Nova Scotia contains 60 rivers which formerly supported populations of Atlantic salmon in the 1950s. The pHs of 13 of these rivers are now <4.7 and no salmon have been caught by anglers from these very acidic rivers since the early 1970s. The catch from the 18 rivers with pH in range of 4.7-5.0 has fallen to approximately 10% of the average 1936-1953 catch. No decline in angling catch attributable to acidification has occurred in rivers whose pH>5.0. In rivers with pH>5.0, juvenile Atlantic salmon were present at population densities which are normal for the region (20-30 fish/100 m^2). No juveniles were found in rivers with pH<5.0 except those that had some tributaries with higher pH (Watt et al 1983).

Intensive chemical (monthly) and biological (annual electrofishing) monitoring of 9 Nova Scotia rivers where Atlantic salmon are threatened with extinction or have already disappeared has occurred since 1980 (Watt et al in prep. b). Data for 1980-86 show declining pHs in 4 of 9 rivers. After 1986, pHs improved so that when examined for the period 1980-88, only 1 river showed an overall pH decline.

4.1b.1.3 WHOLE LAKE EXPERIMENTS*

Whole lake acidification experiments clearly link acidification and fish population losses. Experiments have been conducted in the United States (Little Rock Lake in Wisconsin, Brezonik et al 1986; Watras and Frost 1989) and in Canada (three lakes in Ontario, Schindler 1987).

Probably the best known whole lake acidification experiment is the study of Lake 223 at the Experimental Lakes Area, Ontario (Schindler et al 1985b). Prior to acidification, the average epilimnetic pH was 6.5-6.7 (Linsey and Braun 1984). This pH was gradually lowered to 5.1 during 1976-1981. It was maintained at approximately 5.1 during 1981-1983, and then allowed to rise during 1984-1989.

During acidification, fathead minnow and slimy sculpin (Cottus cognatus), important lake trout food species, became extinct and the remaining fish species (lake trout, white sucker, and pearl dace) had successive reproductive failures (Schindler et al 1985b; Mills et al 1987). By the end of 1983, most lake trout were extremely emaciated because few food organisms remained in the lake. The decline in abundance of each fish species was due primarily to reproductive failures (Mills et al 1987).

The recovery phase of the experiment commenced in 1984. Lake pH gradually rose due to acid neutralization by natural in-lake processes (Kelly et al 1987). During recovery, reproduction of lake trout, white sucker, and pearl dace resumed at pH levels similar to those where reproduction first ceased during acidification (Table 4.1b.3; Mills et al in prep.a; Mills et al in prep.b). Fathead minnow, a species that became extinct during acidification, was reestablished in Lake 223 through emigration from upstream Lake 224.

Other types of experimental manipulation that provided convincing cause/effect evidence of acidification damage are (1) fish stocking and (2) liming experiments (See Section 4.4). Experimental stocking of hatchery fish can act as a large scale bioassay without the artificial features of enclosing fish in cages, providing food, etc. Experimental stocking in lakes with different pHs have shown that low pH causes high mortality of stocked fish (Schofield et al 1986; Gunn et al 1987). For example, mortality of stocked brook trout increases rapidly below pH=5.0 (Schofield et al 1986), a threshold similar to that for population loss in synoptic surveys (Beggs and Gunn 1986). Further proof that acidification causes mortality of stocked fish is provided by subsequent liming of test lakes. After liming, stocked fish generally exhibit high survival and may reproduce in the elevated pH conditions (Schofield et al 1986; Gloss et al 1989; Gunn et al 1990).

4.1b.1.4 INTERACTIONS

While the loss fishes from lakes can lead to subsequent changes in invertebrate communities (Eriksson et al 1980; Stenson and Eriksson 1989), there is also evidence that changes in food web structure can cause changes in fish populations as lakes acidify or recover.

The best known indirect effect of the Lake 223 experimental acidification is the starvation of lake trout at the end of the acidification phase of the experiment. There was a progressive loss of lake trout prey species during acidification (Schindler et al 1985b; Mills et al 1987); most trout became very emaciated and their survival decreased (Mills et al 1987). During the recovery phase of the experiment lake trout condition and survival increased rapidly when populations of prey organisms increased (Mills et al 1990a).

There were three other indirect effects of acidification that contributed to changes in Lake 223 fish populations. First, filamentous algal mats covered lake trout spawning shoals early in the acidification phase of the experiment (Schindler et al 1985b). Lake trout changed spawning areas to shoals not covered with the algae (Mills et al 1987). During pH recovery, lake trout returned to the original spawning shoals (Mills et al in prep.a,in prep.b) after the algal mats receded. Second, fathead minnow was temporarily replaced by pearl dace as the most abundant minnow species during acidification. The increase in pearl dace abundance was likely the result of reduced fathead minnow abundance (Mills et al 1987). Third, white sucker became very emaciated during the recovery phase of the experiment (Mills et al in prep.a). White sucker abundance increased after reproduction resumed during pH recovery, and the population depleted its primary food resource, chironomids (Mills et al in prep.a, in prep.b).

Table 4.1b.3 pH thresholds for onset and reversal of acidification effects on some Lake 223 biota (Schindler et al 1985b; Mills et al in prep. a). Lake 223 was acidified from from pH 6.5 to 5.1 (1976 to 1981), held at pH 5.0 to 5.1 (1981 to 1983), and allowed to recover from pH 5.1 to 5.8 (1984 to 1989).

Change		Average Epilimnetic pH (Year)
Algal Mats:	appear	5.6 (1979)
	recede	5.8 (1988)
Daphnia g. mendotae		
	decreases	5.0 (1981)
	increases	5.5 (1987)
Daphnia catawba		
	increases	5.6 (1980)
	decreases	5.5 (1987)
Pearl dace reproduction (Semotilus margarita)		
	ceases	5.0 (1982)
	resumes	5.4 (1984)
White sucker reproduction (Catostomus commersoni)		
	ceases	5.0 (1981)
	resumes	5.4 (1984)
Lake trout reproduction (Salvelinus namaycush)		
	ceases	5.6 (1980)
	resumes	5.5 (1986)
Fathead minnow reproduction (Pimephales promelas)		
	ceases	5.9 (1978)
	resumes	5.8 (1989)

Further evidence of indirect effects of acidification on fish populations occurred in Whitepine Lake when lake trout recruitment resumed after lake pH increased (Gunn and Keller 1990). Yellow perch were very abundant in Whitepine Lake during the years of greatest acidification and lowest lake trout abundance. As lake trout abundance increased during recovery, perch abundance decreased due to lake trout predation and then lake trout growth slowed.

4.1b.1.2 OTHER BIOTA

Summary: The biomass and productivity of phytoplankton are not reduced by acidification of lake waters. However, at pH<6.0 fewer species are present and the taxonomic composition is altered. A species that produces objectionable lake-water odours may appear. Acidification has changed phytoplankton communities in some lakes of all Canadian provinces east of Manitoba, except Prince Edward Island.

Filamentous green algae occur in shallow shoreline waters of acidic lakes in Ontario, and are a great concern to cottagers. The blooms are clearly linked with increasing lake water acidity. They usually occur when lake water pH is <6.0, and recede when pH rises to ≥5.8.

Acidification causes decreases in the number of zooplankton species in lakes and reduces the average size of remaining species. The total biomass does not usually decrease. Acidification has altered zooplankton communities in some Ontario, Québec, Nova Scotia, and New Brunswick lakes.

Many benthic macroinvertebrates are sensitive to low pH in lakes and streams. Acid sensitive species include some aquatic insects (primarily mayflies, caddisflies, and stoneflies), amphipods, crayfish, snail, clam, and leech species. Losses begin when pH<6.0 and there is evidence of reappearance of some species as lake pH increases. Blackfly populations may benefit from increased acidity.

Many amphibian species that breed in temporary ponds are adversely affected by pH<4.5. The egg stage is generally the most sensitive life stage to low pH while the larval stage is generally more sensitive to high Al levels.

Most effects of acidification on wetland birds occur through changes in quality and quantity of their food resources. Fishes and wetland birds can compete for the same invertebrate fauna in acidified lakes. While some birds may benefit from increased insect abundance when fishes are absent from acidified lakes, several other species have lower reproductive success in acidified lakes and streams. Acidification can also affect choice of habitat for feeding and nesting of wetland birds.

4.1b.2.1 ALGAE

The acidification of lakes is usually not accompanied by reductions in phytoplankton biomass or productivity (Dillon et al 1984; Stokes 1986; Geelen and Leuven 1986; Dixit and Smol 1989). Experimental acidification or neutralization experiments indicate that biomass and productivity either do not respond to changes in pH (Yan and Dillon 1984; Havens and DeCosta 1984; Wilcox and Decosta 1984; Molot et al 1990b, Findlay and Kasian in press, in prep.), or may increase during acidification (Findlay and Kasian 1986; Shearer et al 1987). Increases occur because algal growth in deep water is enhanced (Yan and Miller 1984; Kettle et al 1987), due to increased water clarity in acidified lakes (Yan 1983; Effler et al 1985; Shearer et al 1987).

In contrast to biomass and productivity, the taxonomic diversity of phytoplankton communities is reduced when lake water pH < 6.0 (Stokes and Yung 1986; Siegfried et al 1989; Siver and Hamer 1989; Findlay and Kasian 1986; Havens and DeCosta 1987; Siegfried et al 1989: Siver and Hamer 1989). While chrysophytes and diatoms are the principle contributors to phytoplankton biomass in non-acidic lakes, dinoflagellates and cryptomonads are the principle contributors when lake pH decreases to 5.0 (reviewed by Dixit and Smol 1989). Blooms of Chrysochromulina breviturrita that produce lake-wide, obnoxious odours sometimes occur in lakes of pH = 5.5-6.2 (Nicholls et al 1982; Findlay and Kasian in press), a pH range that produces optimal growth of this species in laboratory cultures (Wehr et al 1985). Diatom and chrysophyte microfossils from recently deposited lake sediments in Ontario, Québec, Nova Scotia, New Brunswick, and Newfoundland show changes in community structure consistent with lake acidification in some lakes for each of these provinces (Charles et al 1990).

Lake acidification often results in increased average size of phytoplankton, often due to increased abundance of large dinoflagellates (Yan 1979; Yan and Stokes 1978; Findlay and Kasian 1986; Havens and DeCosta 1987; Findlay and Kasian in press). Filter-feeding zooplankton cannot easily consume these large algae (Yan and Strus 1980).

4.1b.2.2 PHYTOBENTHOS

Accumulations of filamentous algal mats in acid-stressed lakes affect both lake aesthetics and ecosystem function. In Ontario, cottage owners on 214 lakes indicated that 48% of their lakes had some filamentous algal blooms and an additional 16% of the lakes had extensive blooms (SPR Assoc. Inc. 1986). Seventy-four percent of cottagers reporting algal mats in their lakes indicated these reduced their aesthetic enjoyment of the lake; 88% reported their occurrence reduced the amount of time they spent swimming in the lakes. Filamentous algal mats were particularly apparent in lakes of low alkalinity. While these data are the opinions of cottagers, the opinions appear to be reliable. Ninety-seven per cent of 32 lakes with known filamentous algal problems were correctly identified by cottagers in a pilot study designed to test the accuracy of cottagers' opinions (SPR Assoc. Inc. 1986). Despite many anecdotal references to massive accumulations of algal mats in acidic lakes (reviewed by Stokes 1981), the geographic extent of the problem in Canada east of Ontario is relatively unknown.

Many different algal species may occur in these algal mats. A waterline band develops around a lake perimeter relatively early during the acidification process, at approximately pH=6.2 (Turner et al 1987). This is followed by a second, more extensive growth at approximately pH=5.8 (Howell et al in prep.). The depth distribution and extent of shoreline coverage depends on both level of acidity and season (Howell and Turner in prep.). The primary species are zygnematales green algae, and the principle species is frequently Zygogonium tunetanum (Wei et al 1989). All these algal mats, regardless of taxonomic composition, are considered an aesthetic problem.

The response of these mats to changes in pH are similar. Turner et al (1987) recorded that blooms accumulated on virtually 100% of the shoreline of experimentally acidified Lake 302 when the lake pH was reduced from 6.0 to 5.5. Jackson et al (1990) noted that most of the shoreline of Bowland Lake in Ontario was coated in a band of these algae when pH was in the range 4.9-5.5; the band disappeared completely when the lake pH was raised to 6.3 by liming. During the Lake 223 acidification experiment, the band declined when lake pH increased from 5.4 to 5.8 (Table 4.1b.3, Mills et al in prep.a).

4.1b.2.3 ZOOPLANKTON

Zooplankton biomass in lakes usually is not altered by acidification (Bleiwas et al 1984; Malley and Chang 1986; Siegfried et al 1987). The few reports of higher (Carter 1971; Blouin et al 1984) or lower (Roff and Kwiatkowski 1977; Confer et al 1983) zooplankton biomass in acidified lakes are probably due to differences in trophic status among study lakes rather than lake acidity. However, crustacean zooplankton biomass was reduced in some lakes near Sudbury affected by both acidification and toxic metals from nearby smelters (Yan and Strus 1980; Yan et al in press a).

The number of zooplankton species is lower in acidic lakes than in neutral pH lakes. Zooplankton were surveyed in hundreds of lakes in all provinces of eastern Canada except Prince Edward Island. Lower species numbers were found in acidic lakes in every province except Newfoundland (Table 4.1b.4) where two surveys gave contradictory results (Chengalath et al 1984; Carter et al 1986). Acidification experiments have confirmed this pattern (Schindler et al 1985b; Arvola et al 1986; Havens and DeCosta 1987).

Zooplankton community composition is altered in acidic lakes. During the early stages of acidification species replacements may occur (Malley and Chang 1986), but a net loss of species occurs in the pH range 5.5-6.0 (Table 4.1b.4; Schindler et al 1985b) or even at pH>6.0 (Siegfried et al 1987).

Daphnia galeata mendotae, a widespread species in non-acidic lakes in eastern Canada, is particularly sensitive to acidification. In a survey of 450 lakes in Ontario, Keller et al (submitted) found that this species was almost always very abundant in lakes with pH>6.0, was scarce in lakes with pH in the range 5.5-6.0, and was absent from almost all lakes with pH<5.5. In the experimental acidification of Lake 223, Ontario, this Daphnia

Table 4.1b.4 Summary of information for zooplankton richness from eastern North American surveys.

Source	No. of Lakes	Site	Comments
Bleiwas et al (1984)	7	Ontario	richness reduced at pH<5.5
Carter et al (1986)	142 200	NB, NS Nfld	acid affects community structure no evidence of acid effects
Carter (1971)	32	Ontario	lower richness in acid ponds
Chengalath (1984)	109	Nfld	richness declines with pH
Confer et al (1983)	20	NE-USA	richness declines with pH
Joubert and Tousignant (1983)	158	Québec	diversity and occurrences decline at pH<6.0
Keller and Pitblado (1984)	249	Ontario	richness halved in group with pH 4.7
Kelso et al (1986)	272	E-Canada	richness declines by 25%
Roff and Kwiatkowski (1977)	6	Ontario	diversity drops at pH=5.5
Siegfried et al (1987)	100	NE-USA	richness of plankton declines linearly with pH decline
Sprules (1975)	47	Ontario	richness declines at pH<5.5
Yan et al (1988)	206	Ontario	4 Daphnia species less abundant in acid lakes
Keller and Yan (in prep.)	4	Ontario	richness increased with improved water quality

species disappeared when lake pH was reduced from 5.5 to 5.0 (Schindler et al 1985b). It reappeared in this lake when the pH was allowed to rise again to 5.5 (Table 4.1b.3). Laboratory bioassays using this species confirm its acid sensitivity (Keller et al submitted).

Other species are frequently absent from acidic Canadian lakes. Diaptomus sicilis and Epischura lacustris occur infrequently in acidic lakes (Kelso et al 1986; Joubert and Tousignant 1983), and they disappeared from Lake 223 when the pH was lowered to 5.6 (Schindler et al 1985b). Leptodora kindtii occurs less frequently in acidic lakes (Sprules 1975). The absence of these three large species and other large Daphnia species from acidic lakes coupled with the increased occurrence of smaller acid-tolerant species, such as Diaptomus minutus and Bosmina longirostris (Dillon et al 1984), contribute to low average size of zooplankton in lakes with pH < 5.0 (Keller and Pitblado 1984).

Biological recovery has occurred in some Sudbury lakes after reductions in local industrial emissions of sulfur dioxide and subsequent increases in lake pH (Keller and Yan in prep.). Acid sensitive species, such as Epischura lacustris have recolonized lakes with increased pH (Keller and Yan in prep.; Gunn and Keller in press).

4.1b.2.4 ZOOBENTHOS

There are extensive survey data relating occurrence of aquatic insects to pH in streams in Norway (Raddum and Fjellheim 1984), in the United Kingdom (Harriman and Morrison 1982), Germany (Ziemann 1975; Matthias 1983), the United States (Fiance 1978; Simpson et al 1985), Sweden (Otto and Svensson 1983; Engblom and Lingdell 1984), and Canada (Mackay and Kersey 1985). Thresholds for population loss for Canadian mayfly species are given in Table 4.1b.5.

Amphipods are often absent from acidic lakes. The amphipod Hyalella azteca was absent from lakes with pH < 5.4 in Ontario (Stephenson and Mackie 1986; France and LaZerte 1987), and another amphipod, Gammarus lacustris, was absent from Norwegian lakes with pH < 6.0 (Økland 1980a). Other Gammarus species are also equally sensitive (Økland and Økland 1986).

Some crayfish species are sensitive to acidification. Berrill et al (1986) found two species of crayfish (Orconectes rusticus and Orconectes propinquus) were absent from Ontario lakes with pH < 5.6. The experimental acidification of Lake 223 in Ontario caused the loss of the crayfish Orconectes virilis at pH = 5.1 due to recruitment failures and increased parasitism that started at pH = 5.6 (France and Graham 1985; Schindler et al 1985b; France 1987; Davies 1989). The crayfish Astacus astacus is an important commercial species in Scandinavia that also is sensitive to lake acidification (Økland and Økland 1986).

Fewer snail, mussel, and clam species occur in waters with lower pH, especially Ca poor waters in Canada (Roff and Kwiatkowski 1977; Mackie and Flippance 1983), Norway and Sweden, the United Kingdom, the United States, and Finland (Økland 1980b; summarized

Table 4.1b.5 pH levels at which mayfly nymphs respond negatively to acidification in Canada.

pH	Species	Reference
5.8	Baetis hageni	1
5.6	Baetis brunneicolor	1,3,4
5.6	Baetis pluto	1
5.6	Baetis pygmaeus	3
5.6	Heptagenia hebe	1,3
5.6	Paraleptophelebia mollis	1,3
5.6	Ameletus ludeus	1,4
5.5	Paraleptophelebia debilis	1,4
5.4	Baetis flavistriga	1,3
5.4	Stenonema vicarium	1,3,4
4.7	Stenacron cadadense	3
4.6	Stenonema modestum	1,3
4.6	Eurylophella funeralis	1,3,4
3.5-4.2	Leptophelebia cupida	1,2,4,5

1. Hall and Ide (1987), field survey
2. Hall et al (1988), field transplant
3. Peterson (1989), field survey
4. Giberson and Mackay (submitted), field survey
5. Rowe et al (1989), laboratory bioassay

in Økland and Økland 1986). Studies of the common snail Amnicola limosa in Ontario lakes of differing acidities have shown that newly hatched snails were the most sensitive life stage of this species and growth was reduced in low alkalinity lakes (Rooke and Mackie 1984; Servos et al 1985; Shaw and Mackie 1989).

Leeches were identified as an acid sensitive group by Eilers et al (1984), although few data were present for this group. In a recent Ontario survey, 9 leech species were caught in lakes with pH > 5.5, only 4 species were caught in lakes with pH < 5.5, and no leeches were present in lakes with pH < 4.9 (Bendell and McNicol in press a). Some may view fewer leeches as a beneficial effect of acidification, but leeches are an important food resource for many fish species.

Many benthic macroinvertebrates are lost during experimental acidification. The experimental acidification of Lake 223 in Ontario resulted in the loss of the freshwater shrimp Mysis relicta at pH 5.8-6.0 (Nero and Schindler 1983; Schindler et al 1985b). Several short-term experiments in streams have shown losses of sensitive invertebrates using acid and in some cases Al additions (Hall et al 1980; Zischke et al 1983; Allard and

Moreau 1986; Hall et al 1987; Ormerod et al 1987; Hall in prep. a, in prep. b). Mayfly species lost in these experiments are similar to those lost from streams following long-term acidification (Hall and Ide 1987) and are similar to field survey results discussed previously. Recently, Hall (in prep. b) completed an acidification experiment at the Experimental Lakes Area, Ontario, where there is no appreciable spring pH depression. During the experiment, large reductions in benthic species occurred at more moderate pH levels than in similar experiments conducted in areas of severe spring pH depressions (Hall et al 1987; Hall in prep. a). This implies that many of these other studies were conducted in areas where damage had already occurred.

A valuable case history of changes in benthic invertebrates of an Ontario stream for a 48 year period is presented in Hall and Ide (1987) and Chmielewski (1989). At one stream site where current spring pH fluctuations are small (0.3 pH units), almost all the aquatic insects present in the period 1937-42 were present in 1984-85. However, at sites where large spring pH depressions are currently observed (1.5 pH units), many mayfly and stonefly species that were present 48 years ago, and are also known to be intolerant of low pH, were not present in the 1984-85 sampling. They had apparently been replaced by other, more acid tolerant species. Hall and Ide (1987) concluded that this stream area has acidified in the past five decades.

In a detailed study of blackfly communities, Chmielewski (1989) showed that blackfly emergence has increased almost two orders of magnitude compared to 50 years ago in an Algonquin Park, Ontario, stream where there is a large spring pH depression. Emergence of blackflies in a nearby stream where there is a lesser depression has not changed in the past 50 years. Chmielewski (1989) performed a series of experiments that indicated blackfly larvae could tolerate the low pH levels during spring pulses of acidity.

Some benthic invertebrate populations have reappeared during pH recovery. In Whitepine Lake the number of benthic invertebrate species increased from 39 to 72 when pH increased (Gunn and Keller in press). Many of the colonizing species were acid sensitive organisms, such as mayfly species. Similarly, Hexagenia sp. disappeared from Lake 223 during the acidification phase of the experiment, but quickly recolonized the lake during pH recovery (Table 4.1b.3, Mills et al in prep a).

4.1b.2.5 AMPHIBIANS

Many species of amphibians are potentially vulnerable to elevated levels of acidity and metals. Pough and Wilson (1977) estimated that 30% of salamanders and 50% of frogs used temporary ponds for breeding. These ponds are particularly vulnerable to acidification because of their very low alkalinity (Clark and Euler 1982) and may have pH levels below those in rain or snowmelt (Dale et al 1985; Freda and Dunson 1986). Modest declines in pH (0.2 units) may have substantial effects on amphibian populations in these ponds because significant percentages of ponds are already very acidic (5-10% with pH < 4.5, 15-27% with pH < 5.0 in four Canadian studies, Freda 1986), close to the critical pH of many species (Table 4.1b.6).

Table 4.1b.6 Critical pH levels for embryos of some amphibian species that breed in eastern Canada.

Species	Critical pH	Source
Spring peeper frog (Hyla crucifer)	<5.0	Dale et al (1985)
	4.0-4.2	Gosner & Black (1957)
Tree frog (Hyla versicolor)	3.9-4.3	Gosner & Black (1957)
Wood frog (Rana sylvatica)	4.3	Clark & Hall (1985)
	<4.5	Dale et al (1985)
	4.3	Freda & Dunson (1986)
	3.4	Gascon & Planas (1986)
	3.6-3.9	Gosner & Black (1957)
	3.8	Pierce et al (1984)
	3.5	Tome & Pough (1982)
Leopard frog (Rana pipiens)	3.9-4.1	Gosner & Black (1957)
Pickerel frog (Rana palstris)	5.0	Dale et al (1985)
Green frog (Rana clamitans)	3.9-4.1	Gosner & Black (1957)
Bullfrog (Rana catesbeiana)	4.2-4.3	Gosner & Black (1957)
American toad (Bufo americanus)	4.3	Clark & Hall (1985)
	4.0-4.5	Karns (1983)
	3.8	Dale et al (1985)
Spotted salamander (Ambystoma maculatum)	4.8	Clark & Hall (1985)
	4.5-5.0	Dale et al (1985)
	5.0-5.5	Pough (1976)
	4.0-5.0	Pough & Wilson (1977)

Amphibian embryos are generally more susceptible to low pH than larvae (Freda 1986). Critical pH levels for embryos vary among species, but are generally <5.0 (Table 4.1b.6). This sensitivity is particularly important for species that breed in the early spring because embryos would likely be exposed to the most extreme pH levels at this time (Freda and Dunson 1985b). After hatching, tolerance to acidity increases throughout larval development (Pierce et al 1984; Freda and Dunson 1985a). Direct mortality of larvae can occur after episodic pH depressions in ponds due to rainfall or snowmelt (Gascon and Bider 1985).

While embryos are generally more sensitive to low pH than larvae, recently hatched larvae are more sensitive than embryos to Al (Freda and McDonald 1990). The toxicity of Al for amphibians is highly dependent on water pH. In some species, Al is only toxic at pH<4.5, and in others, toxicity becomes evident at pH>4.5 (Clark and Lazerte 1985, 1987; Dale et al 1985; Andren et al 1988; Freda and McDonald 1990; Gascon et al 1987).

Amphibian surveys were conducted in Nova Scotia, Québec, and Ontario. Dale et al (1985) examined 159 amphibian breeding sites in Nova Scotia but found no correlation between species presence and chemical variables. This may be misleading because only adults of many species were caught, and adults can move between ponds of different pH. Embryos and larvae are more sensitive to acidity and cannot move between ponds. In Québec, fewer wood frog (Rana sylvatica) egg masses occurred in lakes with greater acidity and total organic carbon (Gascon and Planas 1986). Hatching success of three species was negatively correlated with increased Al and acidity during the experimental acidification of a stream. In surveys of Ontario amphibians, Glooschenko et al (1988) observed that spotted salamander (Ambystoma maculatum) and leopard frog (Rana pipiens) were conspicuously absent in areas adjacent to Sudbury where low pH and high levels of Al were found in amphibian breeding ponds. Clark (1986a, 1986b) found the absence of several species of amphibians was related to increased acidity.

4.1b.2.6 WETLAND BIRDS

There is little published evidence indicating direct toxic effects of acidification on wetland birds, though metals mobilized by acidification and passed to birds via the aquatic food chain may cause problems. Nyholm and Myhrberg (1977) reported severely impaired reproduction by flycatchers (Ficedula hypoleuca) feeding on aquatic insects in Sweden. Aluminum obtained from aquatic insect prey was suspected of interfering with normal Ca metabolism (Nyholm 1981). This is the only example of impaired reproduction in wetland birds due to aquatic prey, despite several other studies of bird breeding near acidic waters (see section 4.1b.3.2). However, aquatic biota tend to have lower Al content in more acidic lakes (see section 4.1c.4). Mercury has the greatest potential to present problems for avian reproduction (Scheuhammer submitted), at least in fish-eating species (see Section 4.1c.3).

4.1b.2.6.1 Modifications to aquatic food chains

Most waterbirds rely heavily on high-protein food, particularly small fish and aquatic macroinvertebrates during the breeding season. Consequently, changes in these food organisms caused by direct effects of acidification can cause indirect effects on waterbirds. Modifications that can affect wetland birds are: (1) decreased (or increased) abundance of prey, (2) decreased diversity of prey, and (3) decreased quality of prey.

Many acid-sensitive invertebrates are eliminated at pH levels still capable of supporting fish populations (Mills and Schindler 1986). Insectivorous waterfowl may face poor feeding conditions at these pHs because fish and birds compete for the same residual resources (DesGranges and Hunter 1987; McNicol et al 1987a; Bendell and McNicol in prep.). An acidity-related reduction in the types of available prey has been documented for ring-necked duck (Aythya collaris) (McAuley and Longcore 1988b) and tree swallow (Tachycineta bicolor) (Blancher and McNicol in prep.), two birds that had poorer reproductive success in acidic wetlands.

Feeding conditions for some insectivorous waterfowl species can improve when fish disappear from acidified lakes (e.g. Eriksson et al 1980; Bendell and McNicol 1987). Several waterfowl species, the common goldeneye (Clangula hyemalis) in particular, exploit this situation (Eriksson 1984; Hunter et al 1986; McNicol et al 1987a,c; Bendell and McNicol in prep.).

Birds that have specialized diets are particularly vulnerable to changes in prey populations. Small fish are a preferred food of mergansers and loons (McNicol et al 1987a; Barr 1973) and are often absent or scarce in acidic lakes (McNicol et al 1987a; Parker 1988). When breeding, the dipper (Cinclus cinclus) feeds heavily on acid-sensitive mayfly and caddisfly larvae in nearby streams (Ormerod 1985). In more acidic streams, where fewer of these prey species are available, dipper nestlings are fed less often than nestlings on non-acidic streams (Ormerod and Tyler 1987).

The quality of prey available for birds may be reduced in acidic wetlands. There may be lower energy content of invertebrates (Raddum and Steigen 1981), as well as few non-fish prey with high Ca levels (Blancher and McNicol in prep.; Scheuhammer submitted). Invertebrates that normally contain high concentrations of Ca (e.g. molluscs, crustaceans) are not present in acidic wetlands. Alternative prey may have much lower Ca levels than the same species in higher pH areas (Havas and Hutchinson 1983; Hall et al 1988; Ormerod et al 1988a; Yan et al in press; Scheuhammer submitted). Calcium requirements of growing young birds are in excess of what is available from invertebrates typically found in acidified wetlands (Scheuhammer submitted), forcing birds to obtain these prey elsewhere (Blancher and McNicol in prep). Reduced clutch size and thinner eggshells in acidified environments may also be a response to lower Ca levels in prey (Glooschenko et al 1986; Ormerod et al 1988a; Vickery 1989; see Drent and Woldendorp 1989 for forest birds).

4.1b.2.6.2 Habitat selection

The breeding distribution of many wetland birds reflects the abundance of their prey. For birds whose prey is strongly reduced by acidification, there is evidence for lower breeding densities around acidic waterbodies (Table 4.1b.7). For example, the abundance of breeding dippers (Cinclus cinclus) along streams in Wales is strongly correlated with pH. Dippers select areas with high abundances of invertebrates and these invertebrates are affected by low pH (Ormerod et al 1985, 1986). A historical decline in dippers along the River Irfon paralleled a decline of 1.7 pH units between the late 1960s and 1984 (Ormerod and Tyler 1987). Lower densities of some fish-eating birds occur in acidified areas during breeding (Table 4.1b.7). As noted earlier, the reverse may occur also. Increased insect abundance in acidic lakes, caused by reduced fish predation, can cause an increased density of breeding goldeneye (DesGranges and Darveau 1985; McNicol et al 1987b).

Factors unrelated to acidification, such as the quality of nesting habitat or the tendency for birds to return to the same breeding site, also influence where birds breed. For common loons (Gavia immer) this can lead to apparently inappropriate choices of lakes for breeding, such as acidified lakes that have insufficient fish resources for rearing chicks (Alvo et al 1988; Parker 1988). Tree swallows do not avoid nest boxes erected at low pH wetlands even though this leads to poorer reproductive success (Blancher and McNicol 1988).

4.1b.2.6.3 Reproductive effects on wetland birds

For those birds that do breed at acidified lakes and streams, there are often reproductive consequences. Decreased clutch size, thinner eggshells, later breeding, fewer second clutches, smaller young with poorer growth and lower survival, decreased foraging efficiency, and poorer overall reproductive success are among the effects documented for many species (fish-eaters and insectivores, divers, surface feeders, and flycatchers, see Table 4.1b.7).

Loon reproduction may be either unaffected (Eriksson 1987; Parker 1988) or lowered (McNicol et al 1987b; Alvo et al 1988; Wayland and McNicol 1990) on lakes of high acidity. In a few instances, the decreased abundance of invertebrate prey in acidic lakes can be compensated by (1) increased water clarity that aids feeding, and (2) decreased fish predation on both chicks and remaining invertebrates (Eriksson 1987). The degree of compensation depends in part on the residual abundance of non-fish prey (McNicol et al 1987a), and the extent of reliance on non-fish prey by different species of loons.

Insectivorous waterfowl may have higher or lower reproductive success in acidic wetlands, depending on whether the wetlands have fish populations. Black duck reproduction is at least as good on acidic fishless wetlands as on higher pH wetlands containing fishes (Hunter et al 1986; DesGranges and Rodrigue 1986). In studies where fish status did not differ or was experimentally controlled, lake acidity had a negative effect on waterfowl reproduction (DesGranges and Rodrigue 1986; Haramis and Chu 1987; Rattner et al 1987; McAuley and Longcore 1988a). The worst situation for

Table 4.1b.7 Evidence for indirect effects of acidity on breeding birds (* indicates positive effect of acidity).

Species	Diet/ Foraging	Breeding Distribution	Reproductive Measures	Reference
Common loon (Gavia immer)	Yes	No	Yes, No	1,2,3
Arctic loon (Gavia arctica)			No	4
Common merganser (Mergus merganser)			Yes	5
Kingfisher (Alcedo atthis)		Yes		6
Osprey (Pandion haliaetus)	Yes	Yes	Yes	7,8
Black duck (Anas rubripes)	Yes	Yes	Yes*	9,10,11,12
Common goldeneye (Bucephala clangula)		Yes*		5,10
Ring-necked duck (Aythya collaris)	Yes		Yes	13,14
Dipper (Cinclus cinclus)	Yes	Yes	Yes	15,16,17
Eastern kingbird (Tyrannus tyrannus)		No	Yes	18
Tree swallow (Tachycineta bicolor)	Yes	No	Yes	19,20

References: 1=Alvo et al 1988; 2=Parker 1988; 3=Wayland and McNicol 1990; 4=Eriksson 1987; 5=McNicol et al 1987b; 6=Goriup 1989; 7=Eriksson et al 1983; 8=Eriksson 1986b; 9=Hunter et al 1986; 10=DesGranges and Darveau 1985; 11=Rattner et al 1987; 12=Haramis and Chu 1987; 13,14=McAuley and Longcore 1988a,b; 15,16=Ormerod et al 1985, 1986; 17=Ormerod and Tyler 1987; 18=Glooschenko et al 1986; 19,20=Blancher and McNicol 1988, in prep.

insectivorous ducks appears to be at pH levels just high enough to support fish populations, but low enough to have decreased abundance of macroinvertebrates (DesGranges and Hunter 1987). Such acidic wetlands are probably more numerous than those that have lost fish populations.

4.1c WHAT EVIDENCE EXISTS FOR CONTAMINATION OF AQUATIC ORGANISMS OR AQUATIC DEPENDENT WILDLIFE BY TOXIC SUBSTANCES DERIVED FROM OR RELATED TO LRTAP?

Summary: In the majority of lakes surveyed in Ontario, Hg concentrations of large sport fish exceed 0.5 $\mu g.g^{-1}$ wet weight, the Canadian guideline for unlimited human consumption. Hg levels are also elevated in non-sport fish, particularly in acidic lakes. This phenomenon has not yet been fully explained, but it is likely primarily attributable to increased deposition of Hg from the atmosphere, and to increased availability of methylmercury to fish in more acidic lakes. Elevated dietary Hg levels are a potential threat to fish-eating mammals and birds in Canada; however, the magnitude of the threat is unknown.

Cadmium levels in aquatic invertebrates respond to reductions in pH in a non-linear manner. Concentrations increase as pH levels fall below 6 in response to increases in lake water Cd levels, then decrease as pH falls below about 5, presumably in response to increased competition with hydrogen ions for uptake sites on biological surfaces. Cadmium levels in the livers and kidneys of moose are sufficiently elevated that the public has been warned against consumption of these organs in Manitoba, Ontario, Québec, New Brunswick, and Newfoundland. Regional differences in organ Cd levels in moose exist, but have not been linked conclusively with regional differences in susceptibility of moose habitat to acidification.

4.1c.1 SCOPE

Attention will be restricted to trace metals, Hg and cadmium in particular, in addressing this question. Trace organic compounds of anthropogenic origin are excluded from discussion because of the paucity of field data linking lake water acidity with the accumulation of organic compounds by aquatic biota (Kelso and Gunn 1984). Laboratory studies suggest that such linkages are probable (Fisher 1985a; Fisher and Lohner 1986; Watson and Maly 1987; Ribo 1988); hence, they should be the subject of future Canadian research.

4.1c.2 METAL-ACID LINKAGE

The long range transport of acidic substances is linked with increased exposures of aquatic biota to toxic metals in three ways. First, the metal smelters and fossil fuel-fired power plants that are the principle anthropogenic sources of sulphur also discharge large quantities of trace metals into the atmosphere (Schroeder et al 1987, Nriagu and Pacyna 1988). Anthropogenic emissions of As, Cd, Cr, Cu, Hg, Mo, Ni, Pb, Sb, V, and Zn to the atmosphere actually exceed natural emissions on a global scale (Nriagu 1989). Second, the mobilization of such metals as Al, Cd, and Zn from metalliferous materials in watersheds is increased by the acidification of shallow ground waters (LaZerte et al in

press). Third, acidification of lake waters alters the biogeochemical behaviour of many metals within lakes, often resulting in increased aqueous concentrations of bioavailable forms of metals (Yan and Dillon 1984; Campbell and Stokes 1985; Dillon et al 1988a; Winfrey and Rudd in press).

4.1c.3 MERCURY

Direct evidence of increased Hg concentration in fish in response to the long range transport and deposition of pollutants does not exist. Systematic sampling and analysis of fish from soft water lakes did not commence until the late 1970's, and present records are too short to detect a change in response to the pollutant deposition. However, there are several indirect lines of evidence which suggest that the Hg levels in fish have been elevated either by an increased supply of Hg to lakes from the atmosphere or by an alteration of factors which affect the formation and accumulation of methylmercury by fish.

Mercury enters lakes via precipitation and runoff. For headwater temperate lakes, direct precipitation supplies about half of the Hg, runoff the remainder (Iverfeldt and Johansson 1988; Mierle in press). Mercury in runoff may be derived either from precipitation or from weathering of primary minerals. The relative importance of each is unknown, but only 10% of the Hg in precipitation needs to reach the streams to account for all the Hg in runoff (Mierle in press). Therefore, it seems likely that most of the Hg entering lakes from watersheds is derived from the atmosphere, not from weathering.

The Hg in the atmosphere originates from both natural and anthropogenic sources. Volcanoes, soil and mineral degassing, and emission from the oceans are the principle natural sources (Norton et al in press). The principle anthropogenic sources include emissions from chlor-alkali plants, smelters, and paint plants, and the combustion of fossil fuels and municipal refuse (Andren and Nriagu 1979; Hocking 1979). The current atmospheric Hg concentration is about double the pre-industrial level (Norton et al 1989). Therefore, Hg levels in fish may have increased proportionately simply in response to the increased supply of Hg to lakes from the atmosphere.

Two lines of evidence suggest that the deposition of acidic substances has also increased the concentration of methylmercury in fishes. Surveys conducted in restricted geographic areas, i.e. in areas with uniform atmospheric deposition of Hg, indicate that the Hg content of fish usually increases with increasing lake water acidity. This pattern has been observed for northern pike in Sweden (Björkland et al 1984; Håkanson 1980) and Ontario (Wren et al submitted), brook trout (Sloan and Schofield 1983), white sucker (Hamilton and Haines 1989) and yellow perch (Cope et al in press) in the United States, and yellow perch (Suns et al 1987), smallmouth bass (McMurtry et al 1989), pumpkinseed sunfish (Lapomis gibbosus) (Wren and MacCrimmon 1983), and brook trout and white sucker (Kelso and Gunn 1984) in south-central Ontario. The pattern has also been confirmed by experiment. The experimental acidification of Little Rock Lake in Wisconsin resulted in significant increases in Hg concentration in yellow perch (Wiener et al in press).

Parameters other than acidity may also be correlated with levels of Hg in fishes, and on a province-wide scale, they may account for a larger portion of the observed among-lake variation than lake acidity. For example, the concentration of dissolved organic carbon (DOC), principally fulvic and humic matter, is the best correlate of Hg in several species of fish (McMurtry et al 1989; Wren et al in press). In broad geographic surveys, such natural factors may actually mask the effect of acidity observed in surveys conducted in more restricted areas. Much of our information on the influence of water chemistry on Hg levels in fishes has come from such surveys. The complexity of their interpretation has prevented the development of a widely-accepted explanation for current elevated levels of Hg in fish (Winfrey and Rudd in press; Richman et al 1988).

While the elevation of Hg levels in fishes has not been fully explained, the consequences for fish consumption are clear. Since 1976, the Ontario government has conducted province wide assessments of contaminant levels in fish fillets, publishing the results in fish consumption guides. In most lakes, the large size classes of sport fishes exceed the 0.5 ppm guideline for unlimited human consumption. For example, over 90% of the sampled smallmouth bass and walleye populations and over 60% of the sampled lake trout populations have had at least partial restrictions placed on their consumption. Roughly a third of the sampled walleye populations have a total human consumption ban on the largest size classes of fish. Thus, the contamination of fish with Hg has significantly reduced the size of the edible resource in Ontario.

Piscivores can be intoxicated at dietary Hg concentrations that are frequently observed in sport fishes. Therefore, the elevated levels of Hg often recorded in Canadian fishes may threaten the health of fish-eating birds and mammals. Predators such as eagles, loons, mink, and otters can certainly accumulate Hg from their diets. The survival of mink is reduced at dietary Hg levels of 1 $\mu g.g^{-1}$ wet weight (Wren et al 1987a and b). The reproductive success of loons from the English-Wabigoon River system in northwestern Ontario, a system contaminated with Hg from a local point source, was reduced when prey (fish and crayfish) Hg levels were only 0.3 to 0.4 $\mu g.g^{-1}$ (Barr 1986). Such levels are commonly observed in Canadian sport fish, but Hg levels of the smaller fish preferred by loons have not been well documented. The Hg levels in liver tissue of common merganser ducklings in Algoma averaged 1.1 $\mu g.g^{-1}$ (Scheuhammer submitted), a level comparable with that of loon chicks collected from the Hg-contaminated English-Wabigoon area (Barr 1986).

Unfortunately, the geographic extent or consequences of Hg intoxication of Canadian wildlife can not yet be assessed. The linkages between habitat acidity, dietary Hg levels, and piscivore health are still to be quantified. Mercury levels of birds and mammals from regions of well buffered lakes in Canada are certainly lower than those collected from regions with predominantly soft water lakes (Glooschenko et al 1986; Wren et al 1986). However, small surveys in regions with soft-water lakes have indicated that Hg levels in mink and otter (Wren et al 1986), common goldeneye (Eriksson et al 1989), other duck species (Scheuhammer submitted), and osprey eggs (Eriksson 1986) near acidic lakes are not significantly elevated compared to levels in those species near non-acidic lakes. These species are mobile and probably do not feed exclusively on any single lake. A

thorough analysis of Hg burdens of prey sizes and types normally consumed by particular piscivores is needed to evaluate the health risks to sensitive piscivores in Canada. For loons, such a study should focus on Hg levels of 10-250 g fish (Barr 1973, 1986) .

4.1c.4 CADMIUM AND OTHER METALS

Campbell and Stokes (1985) provide a useful framework for the consideration of the impacts of acidification on the accumulation of metals other than Hg. They hypothesized that the availability of metals to aquatic biota responds to reductions in pH in one of two ways. Ignoring oxide adsorbed phases, type 1 metals (eg. Cd and Zn) undergo little change in speciation over a pH range of 7 to 4, and have relatively weak affinity for biological surfaces. For these metals, acidification should result in a reduction in bioaccumulation because protons out-compete metals for adsorption sites on biological surfaces in acidic lakes. For type 2 metals (eg. Pb), reductions in pH should result in increases in metal bioavailability.

The Campbell and Stokes framework has received much empirical support since it was proposed. Harrison et al (1986) showed that lowering pH from 7 to 5 reduced Zn, Fe, and Mn flux into algae. Yan et al (in press a) demonstrated that zooplankton from Ontario lakes of circum-neutral pH had higher levels of Al, Mn, and Fe than lakes of pH < 5. Bendell-Young and Harvey (1988) showed that larval chironomids from acidic lakes in Ontario had lower Zn and Cu concentrations than animals from less acidic lakes. Hall et al (1988) demonstrated that Ca, Al, and Mn levels of acid-tolerant mayflies and blackflies declined when animals were transferred from streams of pH 6.2 to 4.2. Finally, Krantzberg and Stokes (1988) indicated that Pb levels (a type 2 metal) of chironomids increased monotonically with decreases in pH of Ontario lakes, while levels of Cd, Al, Cu, and Ni in chironomids declined in lakes of pH < 5.

Despite this support for the Campbell and Stokes hypothesis, it is now clear that the accumulation of Cd by aquatic biota can not be understood without consideration of the changes in total aqueous Cd concentrations that accompany depression in lake pH. Campbell and Stokes explicitly excluded consideration of total metal levels. Total aqueous Cd concentrations increase dramatically as lakes acidify (Stephenson and Mackie 1988b). In consequence, Cd concentrations of amphipods (Stephenson and Mackie 1988a), chironomids (Krantzberg and Stokes 1988), mussels (Campbell and Evans 1987) and zooplankton (Yan et al in press c) of Ontario lakes increase as lake pH falls from above 6 to between 5 and 6. However, Cd concentrations of zooplankton (Yan et al in press b and c) and benthic invertebrates (Krantzberg and Stokes 1988; Hall et al 1988) decline as pH falls below 5, despite further increases in aqueous Cd concentration. In summary, Cd bioaccumulation exhibits a non-linear pattern of response to acidification, increasing as pH falls below 6, then decreasing as pH falls below about 5.

For metals other than Hg, there is little evidence that acidification results in increases in metal levels in fish in Canada. A relationship between acidity and Pb levels in fishes has been detected for yellow perch (Suns et al 1987) but not for brook trout or white sucker

(Kelso and Gunn 1984). Bendell-Young et al (1986) and Suns et al (1987) did not observe a correlation between Cd levels in fish and lake acidity; however, such correlations have been observed elsewhere (Andersson and Borg 1988). For birds, the uptake of Cd and Pb increases when dietary Ca is low (Scheuhammer submitted). Since prey with high Ca demands tend to be acid-sensitive (molluscs, crayfish, Daphnia) dietary Ca may be in short supply for birds feeding in acid lakes. Uptake of Cd and Pb may increase as a consequence.

Moose depend in part on aquatic macrophytes for food. Because macrophytes can accumulate Cd from the environment (Miller et al 1983) and moose accumulate Cd through their diet (Frank 1986), Cd levels in moose are elevated in areas with elevated rates of atmospheric Cd deposition (Froslie et al 1986; Crête et al 1987). In fact, liver and kidney Cd levels of eastern Canadian moose are often so high that human consumers have been advised against their consumption in Manitoba, Ontario, Québec New Brunswick, and Newfoundland (Crête et al 1987; Glooschenko et al 1988; Ecobichon et al 1988; Wotton and McEachern 1988; Brazil pers. comm.).

While there are regional differences in Cd levels in Ontario moose, it has not been possible to attribute these differences solely to sensitivity of habitats to acidification. Glooschenko et al (1988) reported that animals inhabiting acid-sensitive terrain in Algonquin Park had the highest liver and kidney Cd levels in their study. However animals from two sites with well buffered soils actually had higher organ Cd levels than animals from the two other poorly buffered sites. In the majority of lakes surveyed in Ontario, Hg concentrations of large sport fishes exceed 0.5 $\mu g.g^{-1}$ wet weight, the Canadian guideline for unlimited consumption. Mercury levels are also elevated in non-sport fish, particularly in acidic lakes. This phenomenon has not yet been fully explained, but it is likely attributable to increased deposition of mercury from the atmosphere, and to increased availability of methylmercury to fish in more acidic lakes. Elevated dietary mercury levels pose a threat to fish-eating mammals and birds in Canada; however, the magnitude of the threat is unknown.

4.2 WHAT PORTION OF AQUATIC SYSTEMS IN REGIONS OF CANADA WILL BE ADVERSELY AFFECTED (CHEMICALLY OR BIOLOGICALLY) AT THE TARGET LOADING OF 20 KG $SO_4^{2-}.HA^{-1}.YR^{-1}$?

Summary: The "critical" load is the wet SO_4^{2-} deposition that does not lead to changes in receiving waters that harm ecosystem structure and function and is determined relative to a pH threshold. In the early 1980s, loss of sport fish species was used as an indicator (translating to a pH threshold of 5.3) and this led to the current target load of 20 $kg.ha^{-1}.yr^{-1}$ wet SO_4^{2-} deposition. Under a uniform deposition of 20 $kg.ha^{-1}.yr^{-1}$, steady-state models predict that the percentage of acidic and low ANC lakes will be much greater than currently observed for all subregions of eastern Canada except south-central Ontario and southwest Québec. The current target load should not be construed as evidence that increasing current deposition up to 20 $kg.ha^{-1}.yr^{-1}$ will not lead to further harmful aquatic effects.

After review of the current information on effects of acidic deposition on aquatic biota (Section 4.1b), pH=6 is now considered a more suitable chemical threshold for use in defining critical loads. Above this pH, most aquatic biota will be protected from harm. However there are some areas in eastern Canada (mainly in the Atlantic provinces) that had a significant percentage of lakes with pH≤6, even under historical conditions and critical load determination must take this into account. Application of steady-state chemistry models permits determination of both critical and higher target loads, the latter implying acceptance of higher damage levels. Critical and target loads determined in this manner do not consider possible aquatic effects associated with episodic acidification.

Variability in terrain sensitivity means that specification of a single critical load for eastern Canada is not appropriate. Critical loads in eastern Canada vary from <8 to >20 $kg.ha^{-1}.yr^{-1}$ wet SO_4^{2-}. Although there is some variability, the Atlantic provinces including Labrador, and eastern Québec generally have very low critical loads (<8 $kg.ha^{-1}.yr^{-1}$). The terrain characteristics of this area dictate a critical load very close to background deposition. Lakes in southwestern Québec and Ontario have critical loads of <8 - >20 $kg.ha^{-1}.yr^{-1}$ reflecting the wide range in terrain sensitivities that exist in each province.

4.2.1 THE "TARGET" LOAD - DEFINITION, HISTORY, AND CONSTRAINTS

An enduring legacy of LRTAP Assessment activities conducted in the early 1980s was specification of a "target" load. It is appropriate to briefly review what must be considered when re-evaluating the target value.

First, it is necessary to differentiate between a "target" and a "critical" load. The latter is a scientific concept that is very young, at least in terms of LRTAP effects. While still evolving, a general consensus for its definition has developed:

> "The highest deposition of acidifying compounds that will not cause chemical changes leading to long term harmful effects on ecosystem structure and function" (United Nations Economic Commission for Europe).

On the other hand, a target load is that deposition set by policy makers for the purpose of environmental protection; it takes into consideration other social, technical, and economic factors that bear on attainment of emission reductions. Hence the target load may differ from the critical load.

The critical load definition above recognizes that more than one pollutant (e.g. both S and N) may contribute to observed effects. However, SO_4^{2-} is the species predominantly contributing to chronic acidification of Canadian waters (see Section 4.1a). Hence it is appropriate to establish a critical load for aquatic systems in terms of this chemical species alone, and emphasis has been and is placed presently on reducing S deposition (via control of anthropogenic SO_2 sources) as the most effective means of achieving environmental protection. The following discussion will focus on SO_4^{2-} although establishing a critical load for N is important for aquatic systems in the longer run, and may to be of greater urgency for other (e.g. terrestrial) ecosystem components. Preliminary consideration of critical N loads has been presented by Nilsson and Grennfelt (1988).

Specification of the critical load is based on prevention of "harmful effects", and these effects may be defined within the context of any ecosystem component . However, the aquatic sector is in the best position to specify or modify the critical load since deposition-response relationships are best understood for the aquatic regime; and protection of the aquatic regime, will in large measure, also result in protection of the remaining natural ecosystem due to the interactions that occur within the terrestrial component prior to water runoff.

US-Canada (1983) reviewed aquatic chemical and biological responses related to wet SO_4^{2-} deposition and concluded that regions receiving ≤ 17 kg.ha^{-1}.yr^{-1} did not exhibit detrimental chemical or biological effects. It should be noted that information available at that time meant the "effects" were generally assessed in terms of observed episodic pH depressions, fish loss or reduced angling success, and in a few instances, indications of long term changes in lakewater pH, SO_4^{2-}, or ANC levels. The critical load inferred from these observations was further quantified through application of the CDR Model (Thompson, 1982) leading to the statement that within the constraints imposed by model assumptions, a "loading of 15-20 kg.ha^{-1}.yr^{-1} wet SO_4^{2-} would maintain surface water pH > 5.3 on an annual basis for basins having cation concentration ≥ 200 μeq.L^{-1} in areas of low runoff". US-Canada (1983) further qualified this critical load by noting that it is in fact spatially variable, that very sensitive basins would not be protected and that future re-evaluation was to be expected as more information was obtained. Based on this information, in 1983 the Canadian Council of Resource and Environment Ministers (CCREM) recognized a 20 kg.ha^{-1}.yr^{-1} target load. Deposition reduction to this level in sensitive regions of southern Ontario and Québec became the guiding principle for a Canadian emission control program now approved by all pertinent levels of government.

Later, the DFO-ESSA model (Marmorek et al 1985) was used by RMCC (1986) to predict that 20 $kg.ha^{-1}.yr^{-1}$ wet SO_4^{2-} deposition would cause a worst case additional loss of 15,000 lakes (i.e. acidification to pH<5). Also, it predicted that a further reduction to 12 $kg.ha^{-1}.yr^{-1}$ would be needed to assure no further losses of highly sensitive lakes and assure recovery of those presently acidified. However, there was no further re-evaluation of the magnitude or allocation of necessary SO_2 emission reductions at the policy level.

Research conducted over the past decade now permits determination of far more reliable critical loads than was possible in the early 1980s and this will be presented in following sections. Note that specification of scientifically based critical loads is the principal focus here, although additional information will be presented to permit policy makers to select differing target loads. When determining critical loads, there are a number of considerations and constraints.

First, the extreme variability in terrain characteristics (bedrock and surficial geology, climate, hydrology, vegetation, etc.) that occurs across Canada means that critical loads are site specific. Definition of a single, critical load for SO_4^{2-} deposition in eastern Canada is not appropriate; the 22 eastern Canadian tertiary watershed Aggregates (AGs, see Section 4.1a.2) have been chosen as the working spatial unit for the critical load determination presented below.

Second, in order to specify a critical load, it is necessary to establish a suitable threshold that defines initiation of "harmful effects on ecosystem and function". We have chosen pH=6 as this threshold (see Section 4.2.1.1).

Third, as was the case in 1983, knowledge of the episodic chemical and biological responses to a given deposition level remains too poorly developed to permit specification of a critical load that accounts for episodic events. Critical loads must still be estimated for steady-state conditions where the chemical and biological responses are better known. Critical loads that consider episodes will be lower in magnitude than those presented below.

Finally, the critical load is defined in terms of wet SO_4^{2-} deposition despite the fact that the environment responds to total deposition (wet + dry). As noted by Henriksen and Brakke (1988), the reason for this is pragmatic. The existing 20 $kg.ha^{-1}.yr^{-1}$ target load is expressed as wet SO_4^{2-}, and wet SO_4^{2-} deposition is easily measured and a national monitoring network already exists. Therefore, the effectiveness of emission control programs in reducing wet SO_4^{2-} deposition to or below critical loads can be directly assessed. Hence the critical load for a region will be evaluated in terms of total SO_4^{2-} deposition and then the value expressed as wet deposition considering relative magnitudes of the wet and dry components. If simple and reliable methods are developed for measuring dry deposition in the future, the critical value can then be expressed in terms of total SO_4^{2-} deposition.

4.2.1.1 CRITICAL LOAD pH THRESHOLD

It seems obvious to define a threshold in terms of biological effects (e.g. loss of a species, diversity reduction, alteration of population structures, etc.); however, in practice such biological indicators have been expressed in chemical terms using suitable transfer functions (see Sections 4.1b and 4.3). The information available to US-Canada (1983) for defining a detrimental biological effect was the loss of sport fish species, which, when converted to chemical terms, gave a threshold pH of 5.3, i.e. the approximate pH required to maintain a bicarbonate buffering system in lakes with low concentrations of base cations. Subsequent research on the pH tolerance of a wide range of aquatic organisms has shown that aquatic ecosystem structure and function is already greatly affected by the time this pH is approached (see Section 4.1b), and a pH threshold of approximately 6 is more appropriate to protect both fish and other aquatic organisms.

It is true that even under pristine conditions, some surface waters likely had pH≤6, and thus the definition of critical load must accommodate this possibility. Hence, the operational definition of critical load for aquatic systems used below will be: the highest SO_4^{2-} deposition that does not increase the percentage of waters having pH≤6. A necessary outcome of this definition is that the critical load will equal the background deposition in areas having lakes with historical pH≤6 although uncertainties in pH prediction must be considered.

Selection of the pH=6 threshold does not imply that no biological effects occur above this pH, indeed some are known. Rather, it should be considered as a prudently chosen value based on the weight of existing evidence on effects. Collection of information in the future that leads to re-evaluation of the actual threshold value should be expected. Using the operational definition of critical load given above, all lakes predicted to have had pH≤6 under background deposition are excluded from the critical load determination although it should be noted that these lakes will also experience biological effects as acidity increases. Finally, target loads evaluated using this definition and threshold value will reflect percentages of lakes exceeding the threshold, but not the absolute degree of exceedence (e.g. whether a given target load will produce a median pH change of 0.2 or 0.8 units for a subset of lakes). Such information exists but presentation of it is beyond the scope of this discussion.

4.2.2 CHEMICAL CONSEQUENCES OF A 20 $kg.ha^{-1}.yr^{-1}$ LOADING

Steady-state models have been used to predict lakewater acidity (ANC and pH) under various SO_4^{2-} loading intensities including the existing 20 $kg.ha^{-1}.yr^{-1}$ target value (see Section 4.3.1). Predictions were made for those sample lakes from each data AG that had complete ion chemistry including DOC (Cl^- not essential for Ontario data). This stringent data selection criterion eliminates a large proportion of the overall data set from the analysis but does permit direct comparison of observed conditions with model predictions. Hence, the data distributions described below only apply to the selected subset of lakes. Recall that predictions are based on total deposition greater than 20 $kg.ha^{-1}.yr^{-1}$ since dry deposition has been added. Dry deposition is assumed to be 15%

of total across eastern Canada (see Part 3 of this Assessment) except for AG 19 (Sudbury-Noranda) where dry deposition approximately equals wet (Dillon et al 1982), and AG 2 (Mid-eastern Nova Scotia) where dry is 35% of total (Shaw 1982).

Using steady-state models (Section 4.3), the effect of imposing wet SO_4^{2-} deposition of 20 $kg.ha^{-1}.yr^{-1}$ on the ANC distribution for each AG compared to that predicted using observed deposition is shown in Figure 4.2.1. The wide variance in AG response to a uniform deposition illustrates why adoption of a single value for the critical load is inappropriate. It should be noted, however, that design of the Canadian emission control program assumed that deposition reduction to 20 $kg.ha^{-1}.yr^{-1}$ level in southern Ontario and Québec would reduce levels in the Atlantic provinces as well. Nevertheless, the single value ignores the fact that the critical load is related to the highly variable terrain sensitivity (see Section 4.1a.1 and Figure 4.1a.1), and may lead to the erroneous impression that areas currently receiving <20 $kg.ha^{-1}.yr^{-1}$ can tolerate greater deposition while in fact the reverse situation is true. For example, AG1-AG11 (the Atlantic provinces, extreme eastern Québec, and Labrador) and AG 13 (Saguenay) currently experience excess SO_4^{2-} deposition of 6-15 $kg.ha^{-1}.yr^{-1}$ (Table 4.1a.2), most are composed of sensitive terrain (except AG 3, 9), and most of the sampled lakes are not acidic (i.e. upper panel of Figure 4.2.1). When receiving 20 $kg.ha^{-1}.yr^{-1}$ (lower panel of Figure 4.2.1), the model predicts that the ANC distribution for these lakes will generally shift to lower ANC values with a higher proportion of acidic lakes.

Central and southern Ontario and southwestern Québec (AG 14-19) currently receive wet deposition (19-25 $kg.ha^{-1}.yr^{-1}$) near the target value and only minor changes in ANC distributions are predicted with imposition of a uniform 20 $kg.ha^{-1}.yr^{-1}$ deposition field. Areas that are less sensitive due to geological conditions (i.e. north and northwestern Ontario, AG 20 and 21; and St. Lawrence South Shore, AG 12; see Section 4.1a.3.1) exhibit only small shifts in ANC distribution due to imposition of 20 $kg.ha^{-1}.yr^{-1}$.

For most AGs, the percentage of lakes having $ANC \leq 0$ within data subsets suitable for modelling (i.e. having complete ion chemistry) is similar to that in the overall dataset (compare column 3 in Table 4.2.1 with the final column of Table 4.1a.3). There are 4 exceptions: AG 1 (Southern Nova Scotia - New Brunswick) and AG 7 (Northern and Southern Newfoundland) in which substantially fewer acidic lakes are represented in the modelling subsets, and AG 19 (Sudbury-Noranda) and AG 22 (Northern Québec) in which the reverse situation exists. Hence, predictions derived from modelling subsets are not expected to be biased towards acidic systems (relative to the overall database) except for AGs 19 and 22.

Comparing the columns for observed and predicted percentage having $ANC \leq 0$ in Table 4.2.1, it is clear that under a uniform deposition of 20 $kg.ha^{-1}.yr^{-1}$, the steady-state percentage of acidic lakes will be much greater than that currently observed for all AGs except those located in south-central Ontario and southwest Québec. Permitting an increase in deposition to the current target load in Atlantic Canada and other areas receiving <20 $kg.ha^{-1}.yr^{-1}$ will cause long term reduction in lake ANC and detrimental effects on aquatic biota. The greatest uncertainty lies with the rate that this would occur, not whether it would occur. Only AGs containing some readily available geological

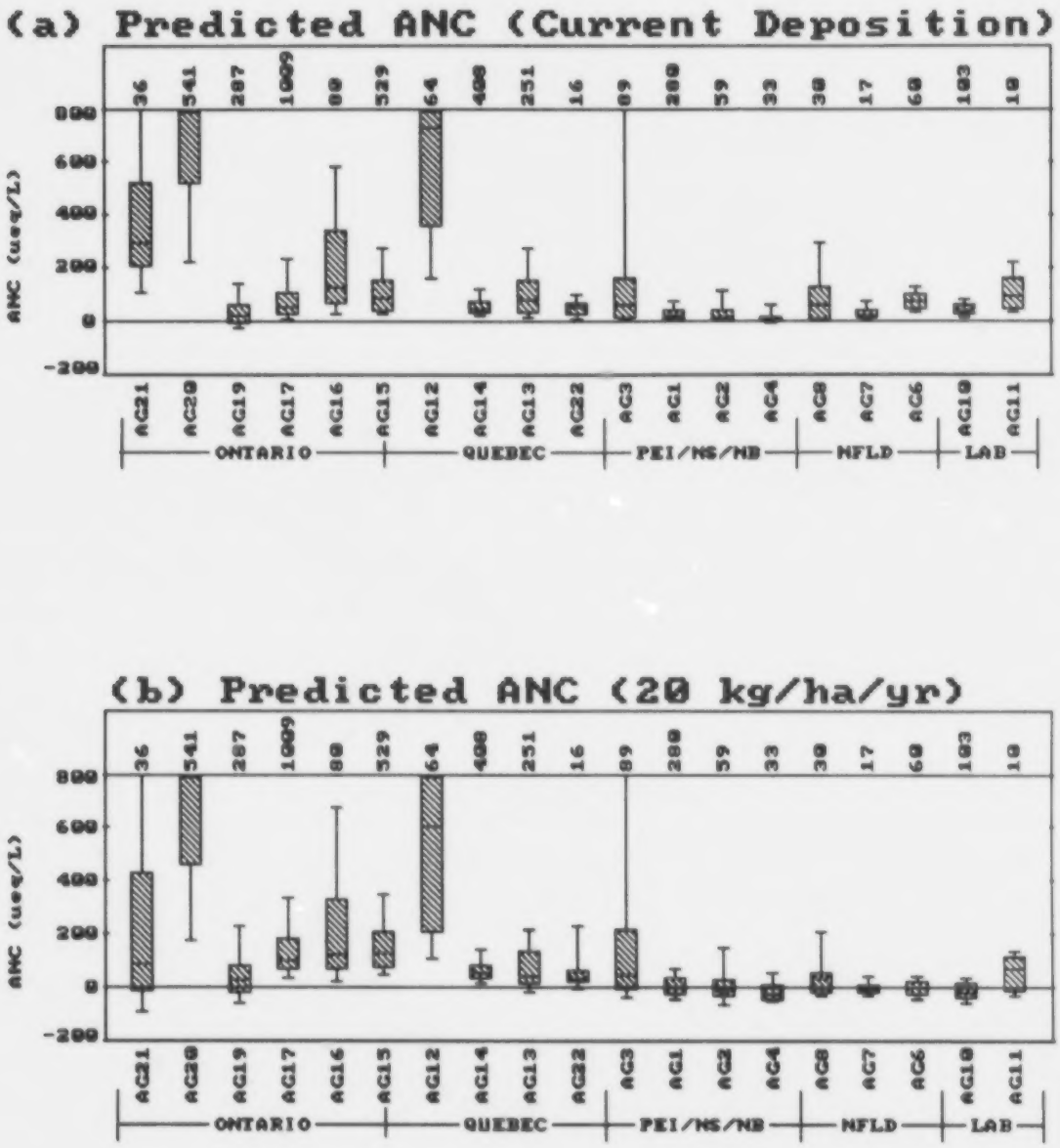


Figure 4.2.1: Boxplots of ANC for AGs of eastern Canada predicted (a) using current deposition, and (b) using wet SO_4^{2-} deposition of 20 $kg.ha^{-1}.yr^{-1}$.

Table 4.2.1 Percentage of sampled lakes within tertiary watershed AGs at or below specific ANC values. Percentages include both those observed under current deposition and those predicted using steady-state models for 20 $kg.ha^{-1}.yr^{-1}$ wet SO_4^{2-} deposition. Only lakes having sufficient data to permit model application have been included.

		Percent Observed (current deposition)		Percent Predicted (20 $kg.ha^{-1}.yr^{-1}$ wet SO_4^{2-} deposition)	
AG#	n	ANC≤0	ANC≤50	ANC≤0	ANC≤50
1	280	14	83	49	84
2	59	10	80	59	85
3	89	1	43	32	55
4	33	36	85	73	88
6	60	0	32	52	95
7	17	6	77	71	100
8	30	7	47	30	70
10	103	1	61	69	96
11	10	0	30	30	40
12	64	0	3	3	8
13	251	2	35	16	57
14	408	0	54	7	46
15	529	1	29	1	14
16	80	0	23	5	24
17	1009	5	47	4	16
19	287	33	72	37	66
20	541	0	1	2	4
21	36	0	0	28	47
22	16	6	44	13	69

sources of buffering (see Section 4.1a.3.1) are predicted to have <25% of sampled lakes with ANC≤50 $\mu eq.L^{-1}$ when receiving 20 $kg.ha^{-1}.yr^{-1}$ wet SO_4^{2-} deposition (last column of Table 4.2.1).

The effect of deposition on lake pH must be predicted to permit comparison with the threshold value (pH=6) during critical load determination. However, the possibility that some lakes had pH≤6 even under background deposition must be considered, and some AGs do exhibit a significant percentage of their lakes in this category (see Figure 4.2.2a for selected examples). This is probably due to the coincident occurrence of high terrain sensitivity (i.e. low capability to supply C_b* and ANC) and sources of natural organic acids (reflected by DOC). Recalling that the operational definition of critical load is that

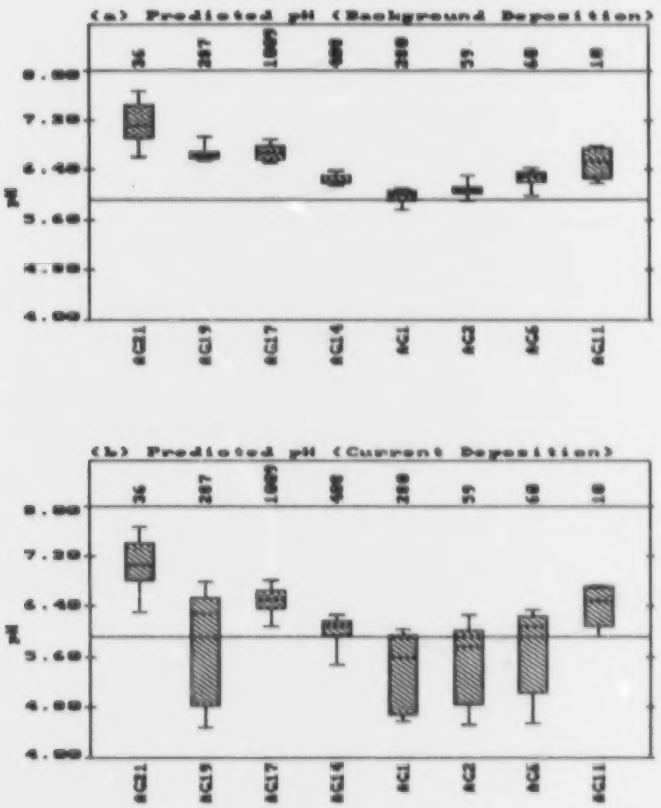


Figure 4.2.2: Predicted steady-state pH boxplots for selected AGs under (a) estimated background deposition, and (b) current deposition.

deposition that does not increase the percentage of lakes having pH≤6, it is important to consider the effect of 20 $kg.ha^{-1}.yr^{-1}$ on the pH distribution of both the entire dataset and the subset that had pH>6 under background or "historical" deposition. Since very dilute lakes in areas with low deposition and little DOC rarely have pH≤6 (e.g. lakes in western USA, Landers et al 1987), it is likely that the subset with historical pH>6 are those lakes little influenced by natural organics. The difference in predicted pH distributions for background and current deposition is seen by comparing the 2 parts of Figure 2.2.2. Note that the distributions apply only to the modelling subsets of data, and therefore, those for current deposition may differ slightly from the observed when the entire database is considered.

Using an estimated background deposition that was spatially variable but generally within

Table 4.2.2 Percentage of modelled lakes predicted to have pH less than or equal to 6 under background deposition (i.e. B%pH≤6). Also presented are pH values from different positions within the pH distributions simulated using the target load of 20 $kg.ha^{-1}.yr^{-1}$ wet SO_4^{2-} deposition. Case "a" gives the 10th and 30th pH percentiles for n lakes, while Case "b" gives the pH value corresponding to 10% and 30% (of n) exceedence of B%pH≤6 (see text for explanation).

			Case a		Case b	
AG#	n	B%pH≤6	10th	30th	B%pH≤6 + 10%	B%pH≤6 + 30%
1	280	52	4.5	4.6	5.7	5.9
2	59	22	4.3	4.4	4.4	4.6
3	89	7	4.0	4.4	4.1	5.5
4	33	42	4.6	4.7	4.7	5.1
6	60	12	4.3	4.5	4.4	4.5
7	17	0	4.8	4.9	same as Case a	
8	30	3	4.6	4.7	4.6	5.9
10	103	13	4.0	4.2	4.1	4.2
11	10	0	4.0	4.0	same as Case a	
12	64	0	6.3	6.9	same as Case a	
13	251	1	4.4	5.9	4.4	5.9
14	408	2	5.6	6.0	5.7	6.0
15	529	0	6.2	6.4	same as Case a	
16	80	0	5.6	6.4	same as Case a	
17	1009	0	6.2	6.4	same as Case a	
19	287	0	4.4	4.7	same as Case a	
20	541	0	7.0	7.4	same as Case a	
21	36	6	4.0	4.0	4.0	5.2
22	16	6	4.6	5.9	4.8	6.0

the range 4-6 $kg.ha^{-1}.yr^{-1}$, lakes having an historical pH≤6 were identified using steady-state models (see Section 4.3). The percent of lakes available for modelling that were predicted to have pH≤6 was calculated (hereafter termed "B%pH≤6") and is presented in Table 4.2.2. The pH distributions under background deposition cover a relatively narrow range compared to that predicted using current deposition (e.g. Figure 4.2.2). The highest B%pH≤6 occurs in AGs 1, 2 and 4 (52%, 22%, 42% respectively); all remaining AGs have B%pH≤6 < 13%. Table 4.2.2 also presents pH values from differing positions within the simulated pH distributions determined for 20 $kg.ha^{-1}.yr^{-1}$ wet SO_4^{2-} deposition. The modelled 10th and 30th percentile pH for all lakes from each AG (Case a in Table 4.2.2) can be compared with the pH value defining that portion of the overall distribution that is 10% and 30% greater than the percentage of lakes having historical pH≤6 (i.e. the percentile value defined by B%pH≤6 plus 10% or 30% of n; Case b). Note that in all subsequent discussion, the adjective "excess", when used in conjunction with the percent

of a modelled pH distribution, will indicate a percentage that is in excess of B%pH≤6.

Comparison of Case a and Case b for AG 1 (South Nova Scotia and New Brunswick) shows that while the overall pH distribution under 20 $kg.ha^{-1}.yr^{-1}$ has large percentages at very low values (e.g. 30% fall below pH=4.6), that proportion with historical pH>6 only declines to values slightly less than pH=6. In contrast, the pHs of lakes having historical pH>6 in AG 2, 3, 4, 6, 10, and 21 are greatly reduced by imposition of 20 $kg.ha^{-1}.yr^{-1}$ wet SO_4^{2-} (i.e. Case b pH values for B%pH≤6 + 10% are similar to the 10th percentile value for Case a). AGs 8, 13, and 22 exhibit intermediate behaviour. Lake chemistry from different regions of eastern Canada respond differently to imposition of 20 $kg.ha^{-1}.yr^{-1}$; this is true not only for the overall data set, but also for those lakes with historical pH>6.

4.2.3 DETERMINATION OF SULPHATE CRITICAL LOADS

As shown in Section 4.2.2, 20 $kg.ha^{-1}.yr^{-1}$ wet SO_4^{2-} will produce steady-state pH levels in many areas of eastern Canada that are below the chemical threshold of pH=6. The critical load for each tertiary watershed AG has been determined using the chemical model described in Section 4.3.1, while at the same time taking into consideration those regions having significant numbers of lakes with historical pH≤6.

The critical load is determined by considering predicted lake pHs for a range of deposition. For example, Figure 4.2.3 shows the predicted distribution of lake pH for AG 14 (Laurentide) and AG 19 (Sudbury-Noranda) for a series of wet SO_4^{2-} loadings (i.e. 8, 10, 12, 14, 16, 18 and 20 $kg.ha^{-1}.yr^{-1}$). Recall that the total deposition actually used to drive the models includes an additional factor to account for the dry component (i.e. 15% of total is added for Laurentide and 50% of total is added for Sudbury-Noranda). For AG14, if ≤10% (excess) of the sampled lakes are to have pH≤6, then the load required to achieve this goal can be read directly from Figure 4.2.3 and is about 12 $kg.ha^{-1}.yr^{-1}$. If ≤25% (excess) of the lakes are to have pH≤6, then it is about 18 $kg.ha^{-1}.yr^{-1}$. Similarly, if ≤10% (excess) of the sampled lakes in AG 19 are to have pH≤6, then the required load is between 8 and 10 $kg.ha^{-1}.yr^{-1}$; linear interpolation within the database used to produce Figure 4.2.3 reveals 8.8 $kg.ha^{-1}.yr^{-1}$. Once again note that the "excess percent" presented here is the percent of the total number of sampled lakes in excess of the percent having historical pH≤6 (i.e. B%pH≤6; see previous Section).

Table 4.2.3 provides target load estimates of wet SO_4^{2-} deposition causing 5, 10, 20, 30, 40 and 50% (excess) of the modelled lakes to have pH≤6. We have declined to present values <8 $kg.ha^{-1}.yr^{-1}$ since the background deposition to estimate B%pH≤6 was 4-6 $kg.ha^{-1}.yr^{-1}$, and >20 since this is the current target load. According to the definition, the critical load is that deposition giving 0% (excess) with pH≤6. However, for those AGs having a small n (<100), it is not possible to assign a deposition to achieve <1% (excess) and therefore the minimum 5% damage level presented in Table 4.2.3. The critical load is less than or equal to the 5% target load value in Table 4.2.3. The target loads quantify the environmental effect (i.e. an increasingly higher damage level) of having to choose for some reason (technological, economic, etc.) a loading higher than that dictated to be

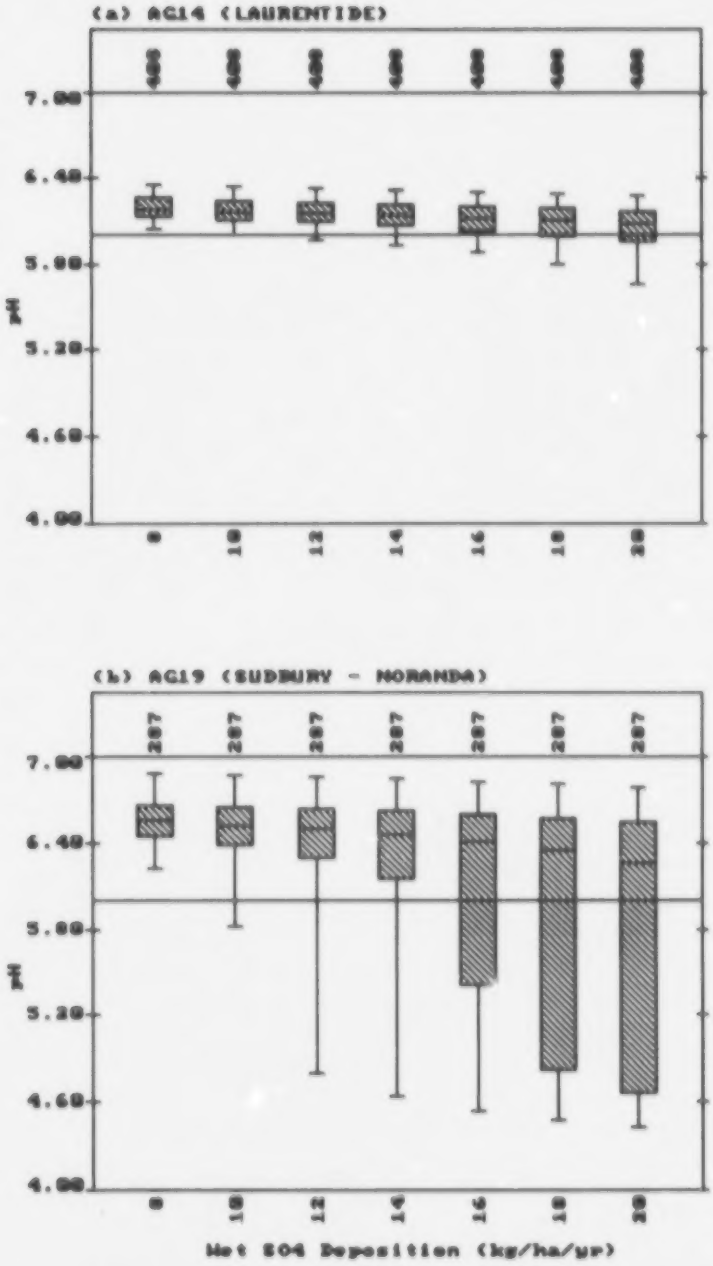


Figure 4.2.3: Predicted pH distributions for (a) AG 24 (Laurentide) and (b) AG 19 (Sudbury-Noranda) for steps of wet SO_4^{2-} deposition from 8-20 $kg.ha^{-1}.yr^{-1}$.

Table 4.2.3 Wet SO_4^{2-} deposition required to achieve pH less than or equal to 6 in 5, 10, 20, 30, 40, and 50% of sampled lakes in AGs of eastern Canada as defined in Figure 4.1a.3 and Table 4.1a.2. The percent values are in excess of the percentage of lakes having predicted historical pH≤6 (i.e. B%pH≤6). A 5% deposition cannot be assigned or inferred for AG 22 due to the low value of n.

AG#	n	B%pH≤6	5%	10%	20%	30%	40%	50%
1	280	52	<8	<8	9	16	>20	>20
2	59	22	<8	<8	<8	<8	8	12
3	89	7	<8	<8	11	18	>20	>20
4	33	42	<8	<8	9	13	16	>20
6	60	12	<8	<8	8	10	13	16
7	17	0	<8	<8	<8	<8	8	12
8	30	3	<8	<8	<8	18	>20	>20
10	103	13	<8	<8	<8	<8	8	10
11	10	0	<8	<8	<8	<8	10	10
12	64	0	13	>20	>20	>20	>20	>20
13	251	1	<8	9	17	19	>20	>20
14	408	2	9	12	17	>20	>20	>20
15	529	0	>20	>20	>20	>20	>20	>20
16	80	0	14	17	>20	>20	>20	>20
17	1009	0	16	>20	>20	>20	>20	>20
19	287	0	<8	9	13	15	19	>20
20	541	0	>20	>20	>20	>20	>20	>20
21	36	6	<8	8	12	18	>20	>20
22	16	6	-	16	18	>20	>20	>20

"critical" by terrain characteristics.

Critical loads in eastern Canada vary from <8 to >20 $kg.ha^{-1}.yr^{-1}$ wet SO_4^{2-}. AG 1 to 11 (all of the Atlantic provinces including Labrador, and eastern Québec) have very low critical loads, i.e. <8 $kg.ha^{-1}.yr^{-1}$ and likely only slightly above the estimated background deposition of 4-6 $kg.ha^{-1}.yr^{-1}$. Terrain characteristics of this area dictate the extremely low critical loads. However, variability in terrain characteristics may produce rapidly increasing target load values for higher damage levels in Table 4.2.3. For example, Northern Nova Scotia - New Brunswick (AG 3) contains extensive agricultural areas of low sensitivity and a target load of 11 $kg.ha^{-1}.yr^{-1}$ leads to 20% (excess) of the modelled lakes with pH≤6 whereas a target load of 9 $kg.ha^{-1}.yr^{-1}$ yields the same damage level in Southern Nova Scotia - New Brunswick (AG 1). A critical load evaluation for smaller geographic units

would reveal this variability although data availability would become a problem.

AGs in southwestern Québec and Ontario have critical loads of <8 to >20 $kg.ha^{-1}.yr^{-1}$ reflecting the wide range in terrain sensitivities present in these areas. In Québec, Dupont and Grimard (1989) proposed 10-15 $kg.ha^{-1}.yr^{-1}$ after analysis of provincial data only, noting that the lower value would be required to protect the most sensitive lake ecosystems. In Ontario, Dillon (pers. comm.) has determined that 8 $kg.ha^{-1}.yr^{-1}$ (as total SO_4^{2-} deposition, wet deposition would be approximately 15% less) is needed to maintain pH>6 for all but 2.5% of its lakes; 15 $kg.ha^{-1}.yr^{-1}$ (once again as total SO_4^{2-} deposition) will protect all but 5% of the lakes. Similarly, Schindler (1988) suggested 9-14 $kg.ha^{-1}.yr^{-1}$ after a general review of aquatic effects. Using a pH threshold of 5.3 and permitting some compensation of SO_4^{2-} increases by base cation increases (i.e. F=0.2), Henriksen and Brakke (1988) determined critical loads of 9-17 $kg.ha^{-1}.yr^{-1}$ for the subregions of the northeastern U.S.A. that are adjacent to Canada. Given the differing bases of evaluation, these estimates of critical loads agree well with those determined here. It is clear that the critical load for many areas of eastern Canada is far below the current target value of 20 $kg.ha^{-1}.yr^{-1}$.

The information in Table 4.2.3 is presented in a different manner in Figure 4.2.4. For eastern Canadian subregions, critical and target loads in classes of 4 $kg.ha^{-1}.yr^{-1}$ are displayed as a function of damage, i.e. percentage exceedence of the pH=6 threshold. The overall length of each horizontal stacked bar corresponds to B%pH≤6, and therefore the regions that have the shortest bars had the highest percentage of lakes with pH≤6 under background deposition. The critical load for a given area lies within that deposition class (defined by the shading) abutting the left hand vertical axis. Also, the deposition class of a possible target load may be ascertained from the shading of the bar for a given subregion that is vertically above a selected damage level (e.g. 10% (excess) of lakes having pH below the threshold). Figure 4.2.4 graphically illustrates the higher damage level that must be tolerated in order to have higher target loads. While the percentage values given here are not population estimates (see Section 4.1a.2.3), selection of even a 10% damage level will correspond to a large numbers of lakes failing to meet the critical load pH threshold. Ten percent of the inventory of lakes >0.18 ha in size south of 52°N latitude and east of 90°W longitude is 79,558.

Also shown in Figure 4.2.4 is the excess percent of lakes failing to meet the threshold under current and Scenario 4 deposition (Scenario 4 is the predicted deposition after all scheduled or expected SO_2 emission control programs in Canada and the US have been instituted, see Section 4.3.2). The emission control programs will reduce the excess percent of lakes failing to meet the threshold for many areas in Ontario and Québec although the damage level remains above 0% in most areas. In the Atlantic provinces, present emission control plans will offer little change from the current situation. Only 5 of 22 subregions in eastern Canada will exhibit ~0% (excess) damage under Scenario 4.

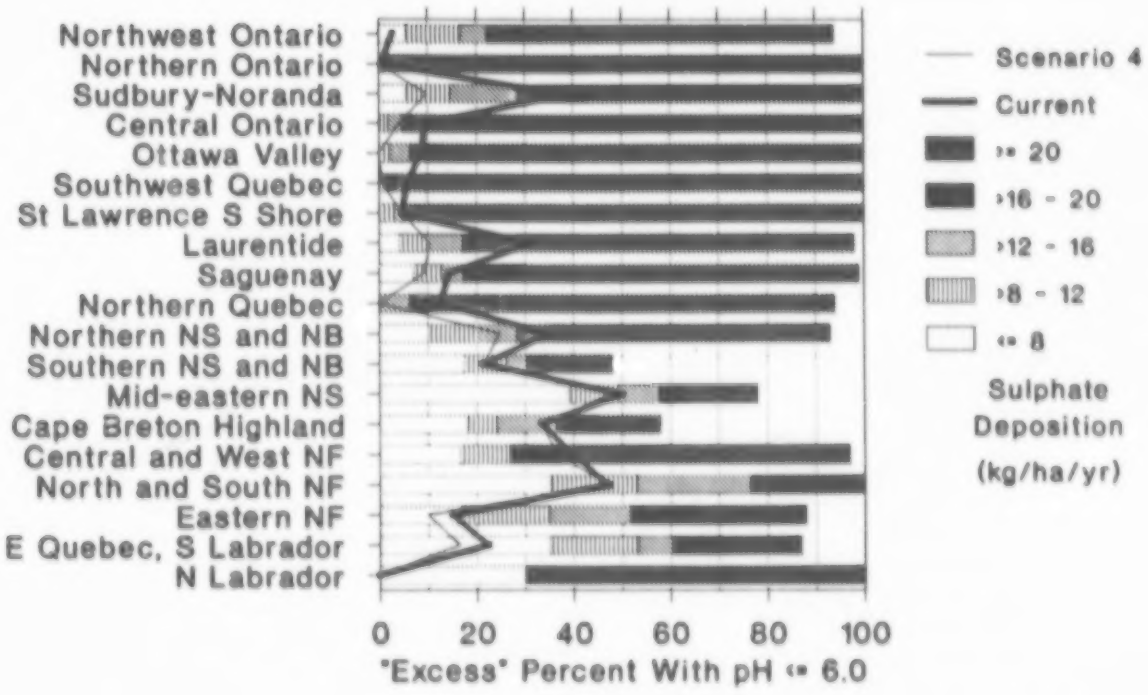


Figure 4.2.4: Relationship between wet SO_4^{2-} deposition (in 4 $kg.ha^{-1}.yr^{-1}$ classes) and excess percent of lakes having pH≤6. Excess percent for 2 deposition Scenarios is shown also (see Section 4.3). Consult text for method of interpretation.

4.3 WHAT ARE THE ANTICIPATED FUTURE IMPACTS OF LRTAP POLLUTANTS ON AQUATIC SYSTEMS, AND WHAT IS THE RATE OF DETERIORATION OR RECOVERY?

Summary: The aquatic effects of four scenarios of SO_4^{2-} deposition were evaluated by mathematical models. Scenario 1 is the observed average deposition over the period 1982 to 1986; Scenario 2 is the deposition projected to occur after full implementation of the Canadian SO_2 emission control program in 1994; Scenario 3 is Scenario 2 plus Phase 1 of the U.S. reduction program (1995) as proposed by President Bush; and Scenario 4 is Scenario 3 plus Phase 2 of the U.S. reduction program (2001).

The regional impact of the 4 deposition Scenarios has been assessed by application of 6 state-of-the-art steady-state models in an expert system framework. Predictions of lake ANC have mean relative errors between 19% to 33%. In general, lake chemistry will improve as SO_4^{2-} deposition is reduced. The degree of improvement depends on the load reduction and the terrain's ability to neutralize acid. There are regions, particularly in the Atlantic provinces, that have lakes with very low base cations and sufficient naturally occurring organic acids to give historic lake pH $\leq$ 6. These lakes require separate consideration when predicting lake effects in terms of a biological threshold of pH = 6.

The models suggest that implementation of the Canadian SO_2 control program will produce improvements in lake chemistry mainly in Ontario and Québec. For example, the Sudbury-Noranda region will have 18% of modelled lakes with pH < 6 under Scenario 2, as compared to 38% under the current Scenario. The proposed U.S. reduction program will benefit this region also; the percentage of modelled lakes with pH < 6 becomes 13% for Scenario 3 and 10% for Scenario 4. Applying these modelled percentages to all the 45,113 lakes > 0.18 ha in size within the region (Section 4.1a), the number of lakes with pH < 6 is estimated to be > 17,000, > 8,000, > 5,000, and > 4,000 for Scenaros 1 through 4 respectively.

Similarly, improvement to the biotic ecosystem is predicted. For example, 21% of the modelled lakes in the Laurentide region in Québec exceed the fish damage level (i.e. have more than a 10% reduction in fish species richness) under Scenario 1. This will be reduced to 14%, 11%, and 8% of the lakes under Scenarios 2, 3, and 4 respectively. In contrast, the models predict little improvements in fish species richness for some regions. For example, 59%, 54%, 51% and 47% of modelled lakes exceed the fish damage level in southern Nova Scotia and New Brunswick for the 4 Scenarios respectively. For nearby northern Nova Scotia and New Brunswick, however, it is at 36%, 30%, 26% and 25%. This large variation in fish species response indicates that biological damages are influenced strongly by terrain characteristics such as soil buffering, sometimes more than by SO_4^{2-} deposition.

The recovery times of lakes are also more dependent on terrain characteristics

than deposition levels. Using dynamic models calibrated with data from several Canadian watersheds, it is estimated that watersheds such as the Turkey Lakes in Algoma, Ontario, may take 50 to 100 years to achieve a new steady state after implementation of emission control programs although improvements in water quality (increases in pH and ANC) will be apparent almost immediately due to the asymptotic nature of the response. Since the data base required by these models is large, only limited application of the models has been possible.

4.3.1 MODELLING APPROACHES

Mathematical models have been used since the early 1980s for the assessment of the impact of LRTAP pollutants on aquatic systems (e.g., US-Canada, 1983). The early models such as the cation denudation rate model (CDR, Thompson 1982) were simple and used the steady state approach. Under the steady state assumption, the ANC in the lake is at equilibrium with the sulphate loading. If the sulphate deposition changes, a new equilibrium ANC must be calculated. In the CDR model, the new equilibrium is governed by only one empirical constant, the F-factor, which is the ratio of the concentration change of major cations (often approximated by $Ca^{2+} + Mg^{2+}$) to the concentration change in SO_4^{2-} in the lake. A large F-factor reflects a large ability to neutralize acidic inputs. While the model seems to provide reasonable predictions if an appropriate F-factor is chosen (Henriksen 1982; Thompson 1986), it is clearly not possible to represent all the acidification processes with only one model constant.

Over the past decade, 2 primary modelling approaches have emerged. One approach is to continue to pursue steady state models by including more relevant processes (e.g. Marmorek et al 1985; Schnoor et al 1986; Dupont and Grimard 1989); the other is to develop models that can simulate the dynamic changes in the chemical concentrations in both the soil layers and the lake. The development of the time-dependent models has been particularly rapid (e.g. Christophersen et al 1982; Chen et al 1983; Cosby et al 1985; Schnoor et al 1986; Kamari 1985; Booty and Kramer 1984; Lam et al 1986). These time-dependent models predict not only the equilibrium concentration in the lake but also the response time and the chemical pathway to reach it. They should therefore be useful for answering the question of future impacts.

However, several factors prevent us from making full use of the time-dependent models for regional impact analysis. First, the time required by a watershed to reach chemical equilibrium with a given SO_4^{2-} load is typically in the order of decades and centuries. Only a few time-dependent models (e.g. Cosby et al 1985) are constructed for such long term computation, although many have demonstrated excellent use for predicting short term episodic events of acidification, particularly those of snowmelt. Computationally it is not economical to run the long term dynamic models merely to estimate the steady state concentration when an improvised steady state model can achieve the same goal (Lam et al 1989a, 1989b). Second, the superiority of the dynamic models lie in using detailed processes such as weathering and in predicting the temporal changes before reaching the steady state. However, little information on weathering rates exists for most parts of Eastern Canada. Third, the biological damage functions available for predicting biological

effects require mean chemical conditions rather than episodic conditions (McNiol et al 1987; Matuszek et al 1988; Minns et al in press; Minns in press; Schindler et al 1989). Fourth, only a few time dependent models (e.g. Rustad et al 1986; Lam et al 1989c) have been calibrated and verified that simulate systems where both inorganic and organic acids are important as is the case in many Eastern Canadian lakes. Most of the other models focus on processes that are not crucial in most Canadian watersheds (e.g. SO_4^{2-} adsorption, Cosby et al 1985).

Thus, care must be exercised in choosing a modelling approach to answer questions on future effects related to specified deposition reductions. It is more efficient to use steady state models than time dependent models to assess the spatial distribution of future chemical and biological effects. Steady state models avoid the uncertainties associated with time varying predictions, and their output is directly compatible with the biological models noted above. In fact, there are several improved steady state models that can be used for this purpose. Instead of choosing only 1 model for blanket application within this assessment, an expert system has been developed for selecting the most appropriate model for each lake according to the available data and a set of rule-based criteria consistent with model assumptions and performance (Lam et al 1988, 1989a, 1989b).

Time-dependent models will be used to provide an estimate of the rate of water quality improvement in response to deposition reductions (long term models) and the probability of episodic acidification (short term models). They will be used on a case study basis for selected watersheds with sufficient information to compare different models, and will demonstrate the uncertainties associated with making such predictions with state-of-the-art models.

4.3.1.1 STEADY STATE CHEMICAL MODELS

Prediction of ANC

There are 2 steady state water chemistry models currently finding extensive usage. First, a refined version of the CDR model (the DFO-ESSA Model, Marmorek et al 1985) was used in an earlier assessment of the effects of acidic deposition on Canadian aquatic ecosystems (RMCC 1986). The refinement involves estimation of the original ANC (i.e. before the onset of anthropogenic acidic deposition) from the present day measurement of major cations. The F-factor is then expressed as a linear function of this original ANC (Marmorek et al 1990). It also includes processes of in-lake ANC generation (Kelly et al 1987).

Second, Schnoor et al (1986) used the mass balance approach and obtained a steady state model (abbreviated TD) that predicts lake ANC from a given input of precipitation amount and acidity. The TD model contains an empirical constant related to weathering (expressed as a function of the acidity, cf. Reuss et al 1986) and cation exchange processes (estimated from measurement of major ions exported from the watershed).

Neither the CDR nor the TD model include an organic acid component. Organic acids are

important in many parts of Eastern Canada (see Section 4.1a.3.3) and must be considered since they are a source of natural acidification. Various models have been suggested for estimating the organic acid content of waters. Oliver et al (1983) proposed a model (abbreviated BO) that relates the organic anion concentration to DOC and pH; recently, Clair and Kramer (submitted) used the uncomplexed form of the organic anions to derive a similar expression for a monoprotic acid. Lam et al (1989c) have proposed a triprotic organic acid model (abbreviated LTH) using a charge density of 4 $\mu eq.mg^{-1}$ C compared to the value of 10 used in BO.

It is possible to link steady state ANC models to the organic acid models, for example, linking the CDR model to the BO model to form a CDR-BO model. Thus, there are 6 possible models: CDR, CDR-BO, CDR-LTH, TD, TD-BO and TD-LTH. Lam et al (1988, 1989a) successfully used predicted ANC values from CDR and TD to select the most appropriate model for a given lake according to 4 basic selection rules; this constitutes the EXPERT model and uses the RAISON expert system. Introduction of an organic acid component extends the EXPERT model and has been achieved by using the BO or LTH estimates but only when the lake is significantly influenced by organic acids as defined by colour >30 Hazen units and/or DOC > 4 $mg.L^{-1}$. That is, for any given lake, if colour <30 or DOC <4 $mg.L^{-1}$, the selection is based on the four rules for selecting CDR or TD, as in Lam et al (1988, 1989a); otherwise, the BO or the LTH model is linked to the selected CDR or TD model.

The approach here is to make use of observed data as much as possible. Inputs to the EXPERT model include wet and dry sulphate deposition, precipitation, and lake concentration of Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}, SO_4^{2-}, Cl, colour and/or DOC. DOC and colour are assumed not to change with SO_4^{2-} deposition. The other ions are used to establish the present day weathering/buffering rates. The model was only applied to those lakes having all these data and satisfying ionic balance (see Section 4.1a.2); model results therefore pertain to these sampled lakes only.

Prediction of pH

Most biological damage models use damage transfer functions expressed in terms of pH (and perhaps Al^{3+}) not ANC. Therefore it is necessary to compute pH from the ANC computed by the EXPERT model and the method of Small and Sutton (1988) was chosen. In this method, the contribution of acidity is based on the charge balance equation, PCO_2 and organic anions. The theoretical equations are fitted against an inverse hyperbolic sine function in order to calibrate the results with observed ANC and pH. In fact, this method has been modified by Dupont and Grimard (1989) into a dose-effect model called SIGMA/SLAM and applied successfully to 1091 lakes in Québec. They reported a concordance coefficient of 0.86 between computed and observed pH, with a standard error of estimation (95%) of 0.27 pH unit. Recently, El-Shaarawi and Nadarisamani (in press) have attempted to use a new statistical distribution in the theoretical equation to obtain a better fit with data from Eastern Canada. Figure 4.3.1 shows some examples of the inverse hyperbolic sine function produced by the Small and Sutton (1988) method fitted to the observed pH and ANC data for AGs 1, 2, 19, and 20. There is a different

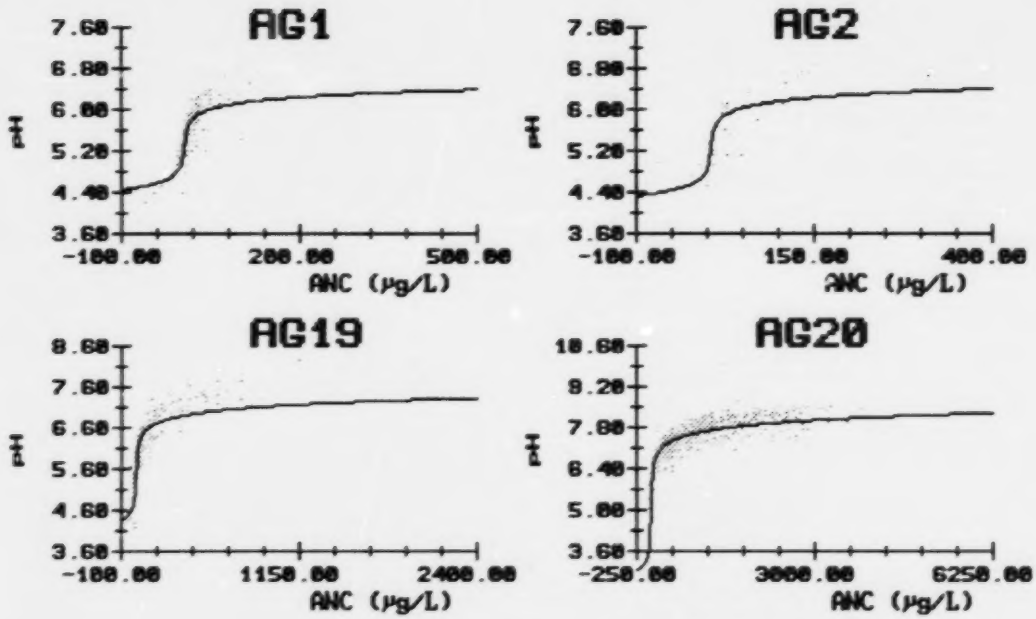


Figure 4.3.1: Examples of pH-ANC relationships including the influence of DOC.

ANC-pH curve fitted from the data for each AG. In each case, the fitted pH is based not only on ANC but also information on the organic anion whenever present in the AG.

4.3.1.2 BIOLOGICAL MODELS

Aquatic biota damage model

Presence/absence data for fish species are available in Canada for developing fish species richness models (Harvey and Lee 1982; Wales and Beggs 1986; Matuszek and Beggs 1988; Mills and Schindler 1986). For example, Matuszek et al (1988) found that fish species number increased with lake area according to the following equation:

$$\log(\text{species number}) = 0.52 + 0.22[\log(\text{lake area})]$$

After filtering out the lake area effects, they then obtained a linear relationship between pH and the mean residual number of species (i.e. reduction in the number of species).

Eilers et al (1984) compiled data (mainly from the USA and Europe) to define the minimum pH at which biological species survive in streams, lakes, or under laboratory conditions. The data compilation covered 7 taxonomic groups of aquatic biota: algae,

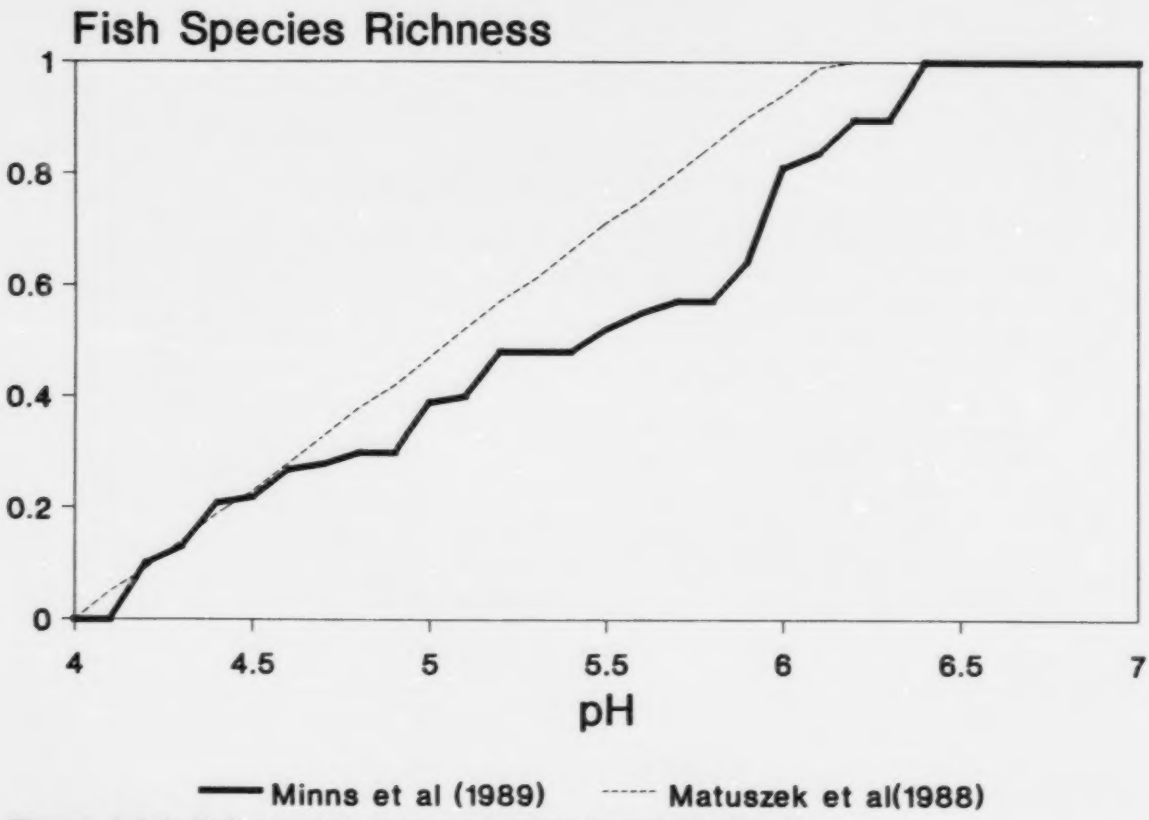


Figure 4.3.2: Fish species richness models based on lake pH.

rotifers, leeches, molluscs, crustaceans, insects and fish (see also Section 4.1b.2). Mills and Schindler (1986) and Schindler et al (1989) have used this information to model biotic damage. Minns et al (in press) further adapted this damage model to perform a regional assessment of species richness in eastern Canada. It should be noted that pH is certainly not the only parameter that affects fish survival; other factors include Ca^{2+}, inorganic Al, and organic acids (Muniz et al 1984).

Figure 4.3.2 shows the fish species richness model of Matuszek et al (1988) and Minns et al (in press). In the Matuszek et al model (derived by interpolation of the data presented in Figure 4.1b.1), the potential species richness is assumed to be 100% at pH=6.1 and 0% at pH=4.0. In the Minns et al model, it is assumed to be 100% at pH=6.4 and 0% at pH=4.1. Hence the primary difference between the 2 models is the pH threshold where effects begin. The Matuszek et al model was developed using Ontario data while the Minns et al model used data from many countries. It was decided to use the Matuszek et al model to assess fish damage in eastern Canada by entering pH computed from the EXPERT chemical model as the driving input. The damage will be expressed as the difference between the percentage of potential species richness

defined by the lake pH under background SO_4^{2-} deposition (cf. original ANC, see Section 4.3.1.1), and the percentage defined by the pH level for a given SO_4^{2-} deposition scenario (see Section 4.3.2). Since it is not possible to verify species richness models, results from the Matuszek et al model will be compared to those from the Minns et al model to obtain some indication of prediction uncertainty.

4.3.2 SULPHATE DEPOSITION SCENARIOS

Four scenarios of wet SO_4^{2-} deposition have been prepared by the Atmospheric Sciences Subgroup (ASSG) for this Assessment. The Scenarios are based on either planned (Canada) or predicted (USA) emission control programs. They will be used to predict anticipated aquatic effects associated with various levels of SO_2 emission control. Detailed description of the assumptions, emission sources, and atmospheric transport models used for the production of these scenarios is given in Part 3 of this Assessment. The deposition scenarios were calculated using 1980 meteorological data throughout with the following differences in SO_2 emissions:

Scenario 1: Determined using SO_2 emissions from 1980 for both Canada and the USA.
Scenario 2: Determined using 1994 Canadian emissions as defined by the Countdown Acid Rain Program; the US emissions were left at the 1980 level.
Scenario 3: Determined using the 5 million short ton reduction in SO_2 emission from US sources (cf. Bush proposal) and the 1994 Canadian emissions.
Scenario 4: This is the same as Scenario 3 except for a 10 million short ton reduction in US SO_2 emissions.

The modelled deposition fields resulting from these Scenarios show that there will be large reductions in wet SO_4^{2-} deposition in south-central Ontario and southern Québec, and much smaller reductions in the Atlantic provinces (see ASSG Report).

The differences in SO_4^{2-} deposition among the 4 Scenarios reflect the likely outcome of differing levels of emission control; however, choosing Scenario 1 deposition to represent the current situation (or base case) is problematic due to the uncertainties arising from modelling errors and the large variability in year-to-year meteorology. For these reasons and also for consistency with the assessment of current status presented in Section 4.1, observed wet SO_4^{2-} deposition averaged over 1982 to 1986 will be used as the base case and taken to be representative of current deposition. This base case will be used as Scenario 1 in the following water chemistry computations. Differences in the predicted deposition fields between Scenario 1 and Scenarios 2, 3, and 4 were applied to the 1982-1986 data to obtain as realistic deposition fields as possible for each level of emission reduction. Wet SO_4^{2-} deposition for each lake station was then interpolated for each Scenario using the RAISON expert system (Lam et al 1989a). Similarly, the precipitation amount and chemistry data were interpolated for each lake for use as inputs to the aquatic chemistry models. The terrestrial and marine components of the background SO_4^{2-} deposition that are required by aquatic chemistry models were derived from the 1982-1986 Ca^{2+} and Mg^{2+} deposition (Marmorek et al 1985). Dry deposition was assumed to be 15% of the total (see ASSG Report for rationale), except AG 19 (Sudbury-

Noranda) with 50% dry deposition (Dillon et al 1982), and AG 2 (mid-eastern Nova Scotia) with dry as 35% of total (Shaw 1982). We assume that the same dry to total deposition ratios hold for all Scenarios.

4.3.3 MODEL CALIBRATION AND SENSITIVITY ANALYSIS

The 6 models discussed in 4.3.1.1 were calibrated with Canadian data and the coefficients adjusted on a lake-to-lake basis by using observed data wherever possible (e.g. the F-factor defined by measured cation concentrations, see Marmorek et al 1990). Figure 4.3.3 shows median ANCs computed by the 6 models using average 1982-86 SO_4^{2-} deposition as the driving variable; only data for AGs having observed median ANCs between 0 to 100 $\mu eq.L^{-1}$ are shown. Comparison of simulated with observed data shows

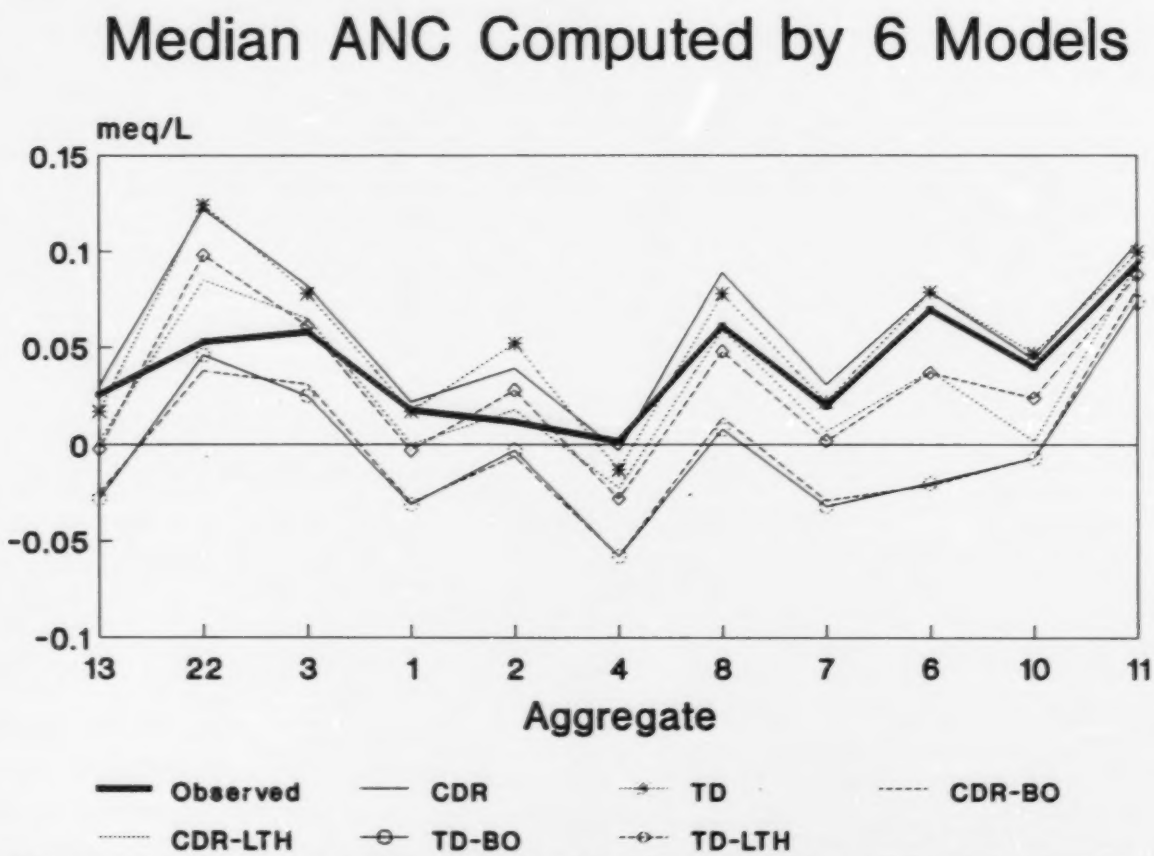


Figure 4.3.3: Examples of ANC results predicted by individual and linked lake chemistry models (CDR, Thompson 1982; TD, Schnoor et al 1986; BO, Oliver et al 1983; LTH, Lam et al 1989c) for selected AGs.

that it is difficult to choose just one model to apply to all AGs. Models with an organic acid component (e.g. CDR-BO) generally predict a lower ANC than those without it (e.g. TD), as expected. Observed ANCs are generally within those computed by the six models (Figure 4.3.3). While further fine tuning of model coefficients is possible, results obtained with the original calibrated coefficients were deemed adequate for the purpose of model selection with the expert rules defined in Section 4.3.1.1.

Figure 4.3.4 shows ANC box plots (see Section 4.1a.3 for description of box plot characteristics) produced by the EXPERT model under the current deposition Scenario (e.g. 1982-86 base case Scenario); observed lake ANC is presented also for comparison. Results for AG 20 and 9 are not shown in Figure 4.3.4 because the ANC values are higher than 0.4 meq.L^{-1}. The predicted ANC distributions (i.e. the box position and size) generally compare well with the observed indicating that the EXPERT selection rules are correct (particularly for the low ANC lakes), and inspiring confidence in its subsequent application for other deposition Scenarios. For southern Québec (mainly AG 12, 13 and 14), Lam et al (1989a) determined a mean relative error of 22% for the EXPERT results,

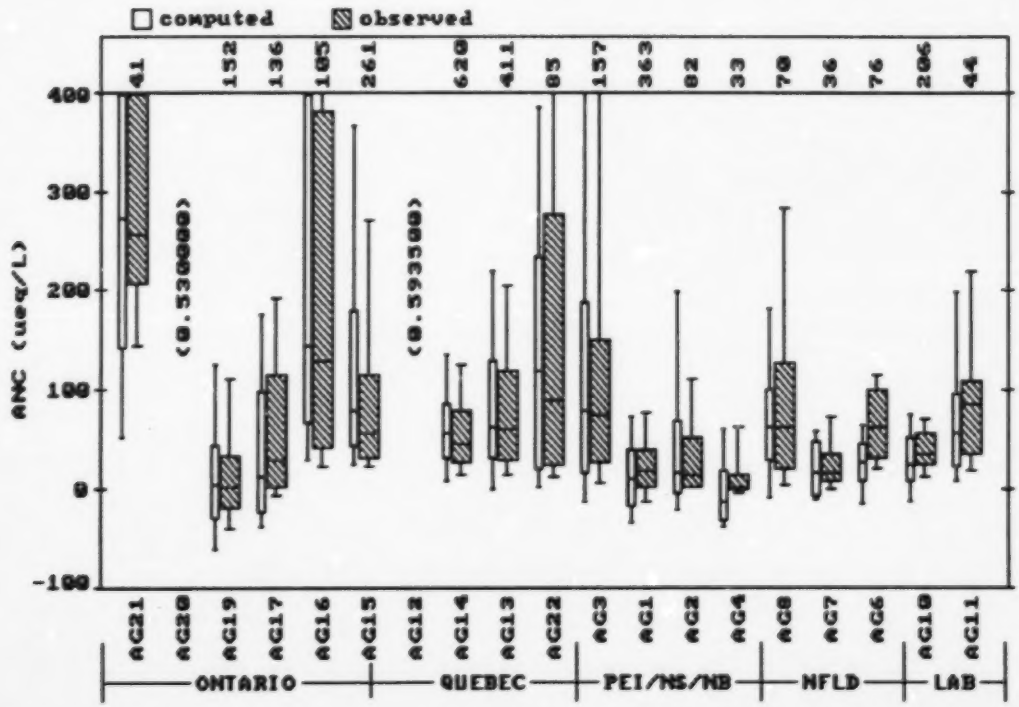


Figure 4.3.4: Observed vs computed (Expert model) ANC boxplots. The number of modelled lakes for each AG is at the top; the numbers in brackets are observed medians >0.4 meq.L^{-1}.

compared to 39% and 75% for the individual results of CDR and TD, respectively. Similarly, Lam et al. (1989b) found a mean relative error of 19% for EXPERT compared to 22% and 78% for CDR and TD using New Brunswick data (AG 1 and 3).

To verify the EXPERT model, data previously not used in the calibration were compared with the model results. There are a large number of stations in AG 15, 16, 17 and 20 which have no Cl^- data and therefore where excluded from the analysis presented in Figure 4.3.4. Since these stations fall in Ontario, marine influences and therefore lake concentrations of Cl^- are considered negligible. The mean relative error is 33% for this set of data. Thus, based on these tests, the EXPERT model results are within the variability of observed ANC data (Figure 4.3.4). Seventeen lakes had both the data necessary for predicting lake pH using estimated background deposition and paleolimnological inferences of historical pH; a linear regression to compare these data was significant at $p=0.02$.

Finally, Lam et al (1989b) determined that the model predictions are sensitive to (in decreasing order): terrain sensitivity, the CDR F-factor, the partition criteria used in the selection rules, SO_4^{2-} deposition, and the TD weathering rate. The model is more sensitive to organic acid parameters such as charge density and equilibrium constants than the SO_4^{2-} loading input (Lam et al 1989c). Prediction uncertainties of the individual models and the combined model are greater for higher SO_4^{2-} inputs but become smaller for reduced loads (Lam et al 1989a).

4.3.4 PREDICTED CHEMICAL EFFECTS: SCENARIOS 2, 3 AND 4

As discussed in Section 4.3.1, a salient feature of the steady state approach is the standardization of chemical effects for different deposition Scenarios. The impact on each lake can be measured by the steady state value of ANC or pH, which is at equilibrium with the given loading. If time dependent models were used, the time factor would become a complicating factor in the standardization, i.e. different concentrations could be reached at different times.

Figure 4.3.5 shows predicted pH for current deposition and for Scenarios 2, 3 and 4 respectively. The computed "excess" 10% pH for each AG was used to demonstrate regional differences (i.e. the pH of that lake in the overall predicted pH distribution that is 10% in excess of the percent having historical $pH \leq 6$, see Section 4.2.2 for elaboration). For example, the excess 10% pH in AG 19 (Sudbury-Noranda) was predicted to increase from <4.5 under current deposition to >6 under Scenario 4 deposition. On the other hand, the excess 10% pH in AG 1 (southern Nova Scotia-New Brunswick) will change little for the same Scenarios.

Figure 4.3.6a shows the predicted excess percentage of lakes with $pH<6$ for the 4 deposition Scenarios. The excess percentage of lakes in AG 19 (Sudbury-Noranda) with $pH<6$ is 38%, 18%, 13% and 10% for current, Scenario 2, 3, and 4 deposition, respectively, while for AG 1 (southern Nova Scotia - New Brunswick), it is about 21% in all 4 cases. Figure 4.3.6b shows equivalent information for lakes with $pH<5.5$ (i.e. AG

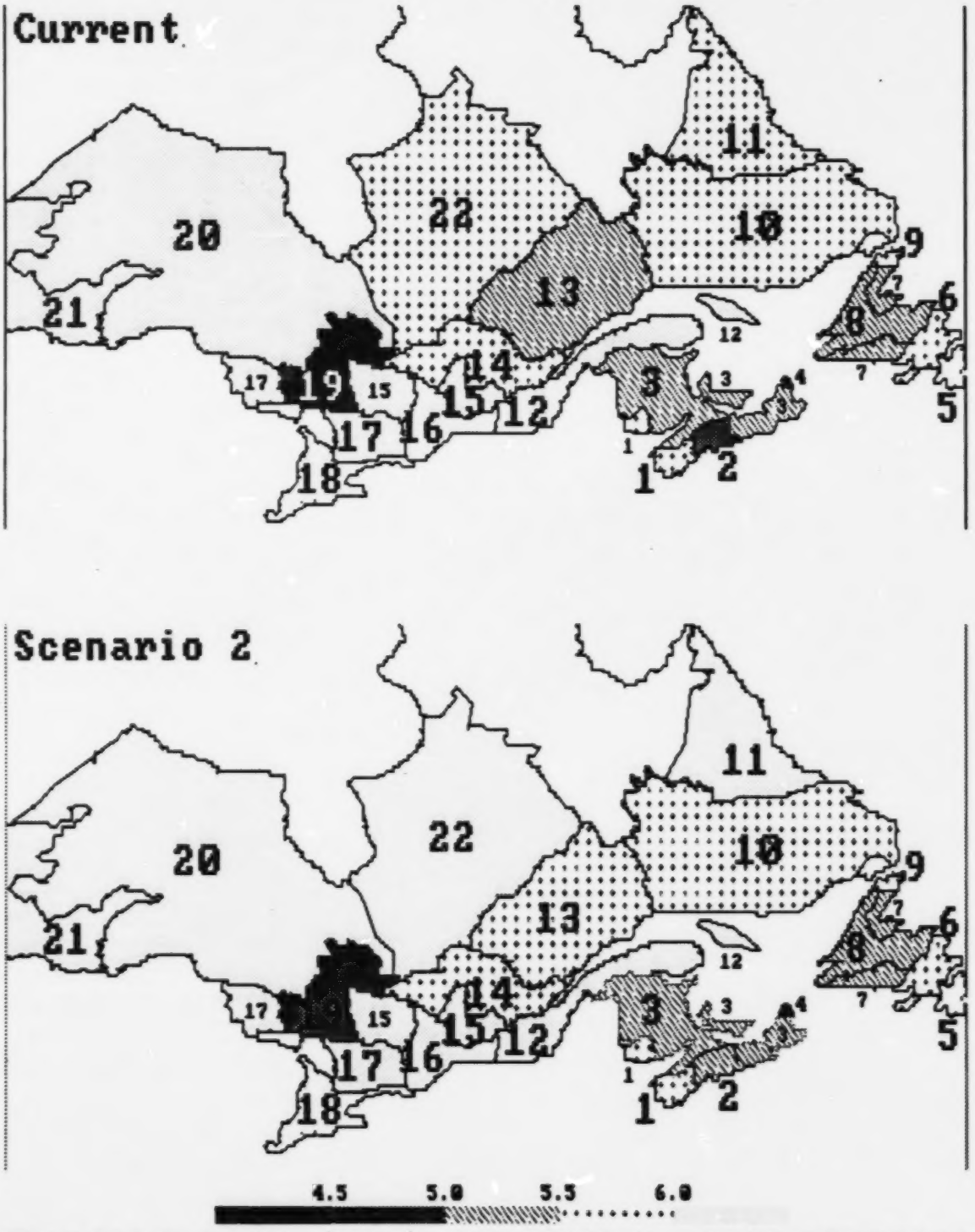
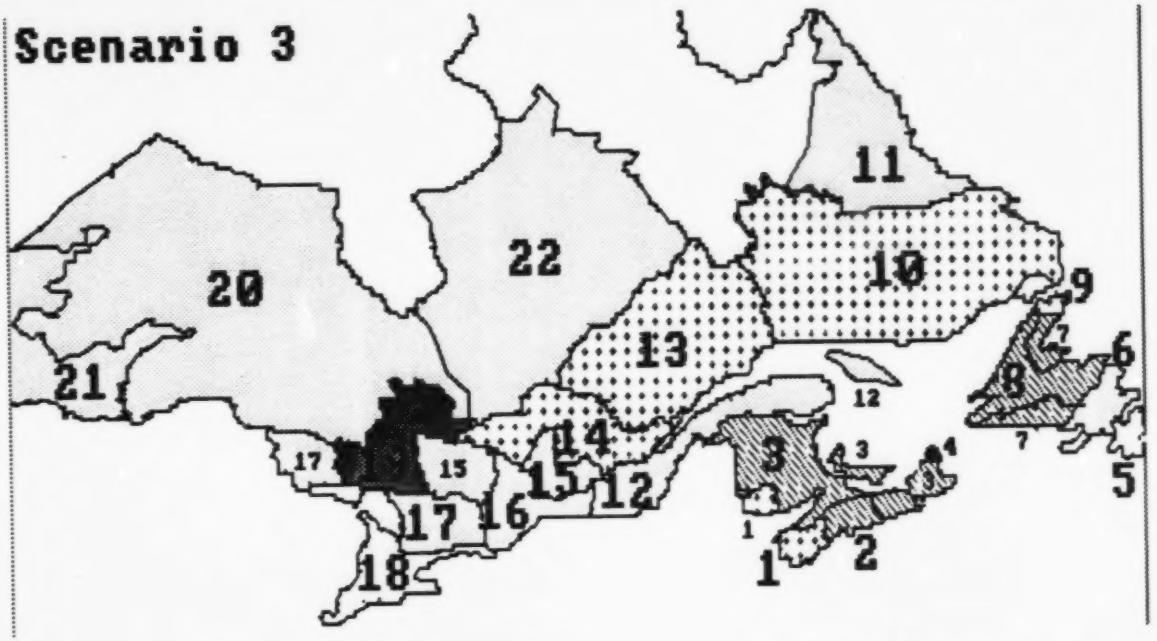


Figure 4.3.5: Predicted lake pH for the excess 10% lake in each AG (see Section 4.2.2 for the meaning of "excess") under the 4 deposition Scenarios specified in Section 4.3.2.



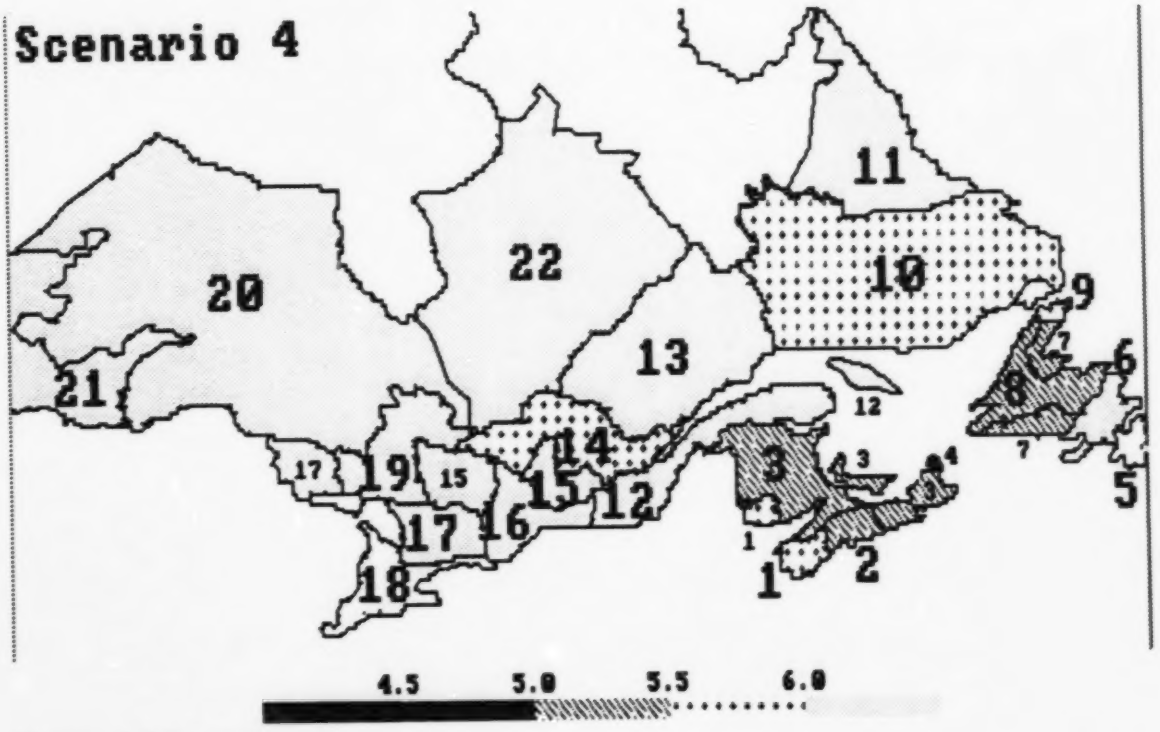


Figure 4.3.5: continued

19 has 32%, 16%, 12% and 8% of lakes with pH<5.5 respectively, while AG 1 has about 5% in all 4 cases). Hence, while most lakes in the Sudbury-Noranda AG had background pH>6 (B%pH≤6 = 0 in Table 4.2.2), they are also very sensitive to SO_4^{2-} deposition leading to the high excess percent pH<6 (even pH<5.5) at current values and the great pH recovery under Scenarios 2, 3, and 4. In contrast, while over half the lakes in southern Nova Scotia - New Brunswick had historical pH≤6 due to very low base cations in combination with natural organic acids (B%pH≤6 = 52 in Table 4.2.2), those that originally did have pH>6 rarely fall below pH=5.5 even under current deposition. This is consistent with the critical and target load analysis presented in Section 4.2.

The predicted excess percentages provide only an estimate of the relative damage within an AG but it should be noted that the number of lakes involved may be large. For example, AG 19 (Sudbury-Noranda) contains 45,113 lakes >0.18 ha in area, and extrapolation of the above results to this overall lake inventory suggests that the number of lakes with pH≤6 in excess of those having historical pH≤6 would be >17,000, >8,000, >5,000, and >4,000 for current, Scenario 2, 3, and 4 deposition respectively. The accuracy of the numbers presented here is unknown since the database and the modelling subset do not statistically represent the inventory; however, as discussed in Section 4.1a.2.3, the database is not likely to over-estimate the magnitude of lake acidification.

The modelling results demonstrate the benefit of SO_2 emission reduction programs. In most AGs, lake chemistry will improve as the SO_4^{2-} deposition is reduced. The degree of improvement depends on the load reduction and the terrain's ability to neutralize acid. For example, the improvement in AG 19 (Sudbury-Noranda) is greater than AG 10 (eastern Québec - southern Labrador, see Figure 4.3.6a) because reduction in SO_4^{2-} input is greater in the former although both have acid sensitive soils. On the other hand, while AG 12, 13 and 14 (southwestern regions of Québec) are adjacent and subject to similar deposition reductions, the response of lake pH is different (Figure 4.3.6a). AG 12 (St Lawrence South Shore) experiences the least change since its soils are well buffered and the chemical damage is initially small, while AG 14 (Mauricie) shows the greatest improvement in lake pH because its terrain is more sensitive. For remote areas such as AG 11 (northern Labrador), 20, 21, and 22 (northern Ontario and Québec) the chemical damage levels are low and the response to different reduction scenarios is predictably small (Figure 4.3.6a). Because of the widespread occurrence of highly sensitive terrain, there will be a greater proportion of lakes with low pH in the Atlantic Provinces compared to Ontario and Québec, even after the effects of organic acids (Howell 1989) have been largely accounted (i.e. by using percentages in excess of B%pH≤6). Note that all pH computations involved the use of a regional relationship between ANC and pH that included the influence of organic anions if present (Section 4.3.1.1); organic anions may still affect those lakes with historical pH>6.

The spatial resolution of the results presented in Figures 4.3.5 and 4.3.6 is at the watershed AG scale. A finer resolution (i.e. at the tertiary watershed scale for southeastern Canada) is discussed in Lam et al (1988, 1989a, 1989b). Lam et al (1988) presented a regionalization procedure in which statistical distributions of observed data and model results are used to derive the lake ANC distribution for watersheds with

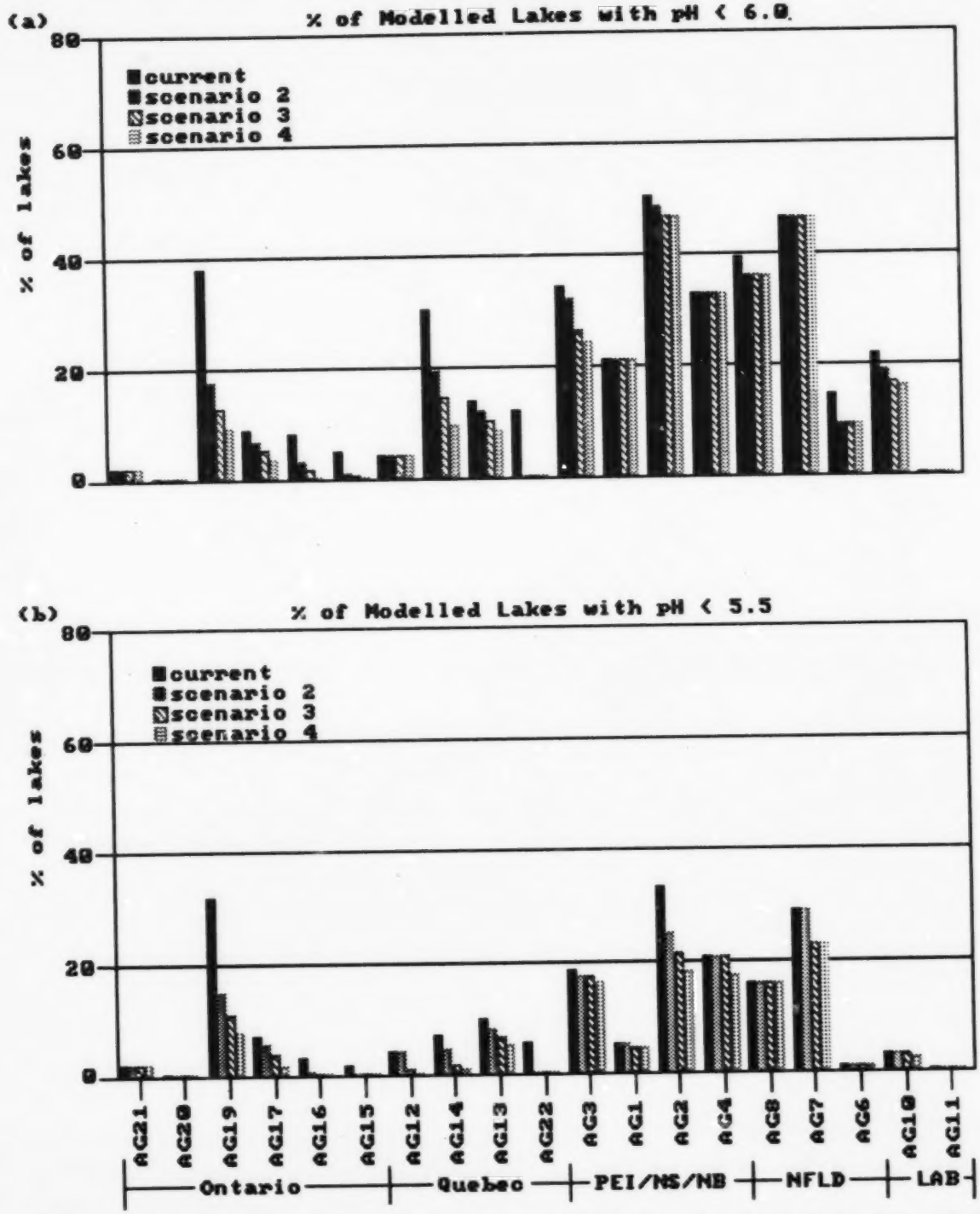


Figure 4.3.6: Predicted excess percent of modelled lakes having (a) pH≤6.0 and (b) pH≤5.5 within each AG for the 4 Scenarios of SO_4^{2-} deposition.

insufficient data for running the model. Based on these results, there are differences in the predicted 10th percentile pH of the watersheds within a particular AG. For example in AG 3 (northern New Brunswick, Nova Scotia and PEI), the excess percent is 35%, 33%, 27%, and 24% (Figure 4.3.6a) for the 4 Scenarios respectively; however, within this AG, several tertiary watersheds (e.g. in PEI) having well buffered soils show 0% in all cases (Lam et al 1989b).

4.3.5 PREDICTED BIOLOGICAL EFFECTS: SCENARIOS 2, 3 AND 4

The effect on aquatic biota is based on the computed steady state pH for each sampled lake under different Scenarios using the biotic damage models (Section 4.3.1.2). Hence, for each deposition Scenario, damage is estimated by the difference between computed potential species richness and the original potential species richness computed at background deposition. Since damage determined in this manner is based on a difference, there is no need to restrict the analysis to lakes having historical pH>6, and therefore, prediction of biological effects uses the entire modelling database. For example, Figure 4.3.7 shows results of the Matuszek et al (1988) model for each deposition Scenario, and gives the percentage of sampled lakes in each AG having ≥10% fish damage. Greater than or equal to a 10% reduction in potential fish species richness will be used extensively in the following discussion and will be referred to as the "fish damage level". As expected, estimates of regional fish damage are similar to the Scenario figures for pH (Figures 4.3.5 and 4.3.6). For example, >20% of the sampled lakes in AGs 1, 2, 3, 4, 7, 8 exceed the fish damage level for Scenario 2 (Figure 4.3.7). These AGs are the same as those with >20% of lakes with pH≤6 for Scenario 2.

According to results from the Matuszek et al model (Figure 4.3.7), improvement in fish species richness occurs, for example, for AG 10 (Eastern Québec - Southern Labrador), AG 14 (Laurentide) and AG 19 (Sudbury - Noranda) between current deposition and Scenario 2, i.e. the deposition reduction arising from the Canadian emission control program. Similarly, improvement is predicted for AG 2 (Mid-eastern Nova Scotia) between Scenarios 2 and 3, i.e. reflecting the effect of proposed U.S. emission control programs. Note that these improvements reflect only those defined by the fish damage level and lake percent intervals presented in Figure 4.3.7. In general, improvements are possible in other regions and for other ranges of damage levels.

Figure 4.3.8 further illustrates regional variability in the fish damage level resulting from the 4 deposition Scenarios. For example, the number of sampled lakes exceeding the fish damage level in AG13 (Saguenay) is reduced from the current condition of about 14% to 12%, 11% and 8% for Scenarios 2, 3, and 4, respectively. Both the Canadian and the U.S. reduction programs are effective for reducing the effect on fish species in this region. Similarly, for AG14 (Laurentide), the current damage level of about 21% is reduced to 14%, 11% and 8% respectively.

In contrast, some regions do not exhibit great improvements in fish species richness.

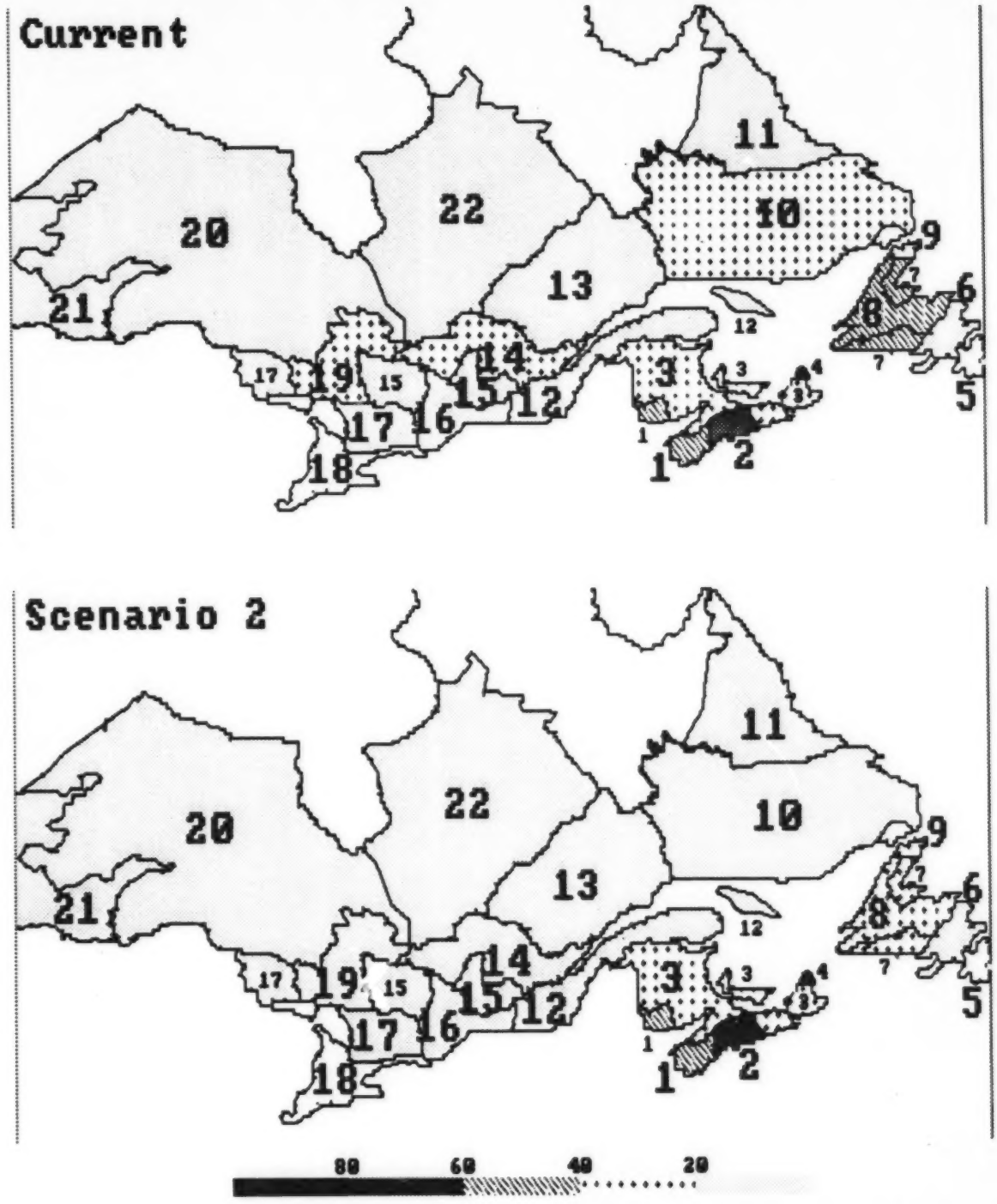


Figure 4.3.7: Predicted percent of lakes exceeding the fish damage level (i.e. ≥10% reduction in fish species richness) under the 4 deposition Scenarios specified in Section 4.3.2.

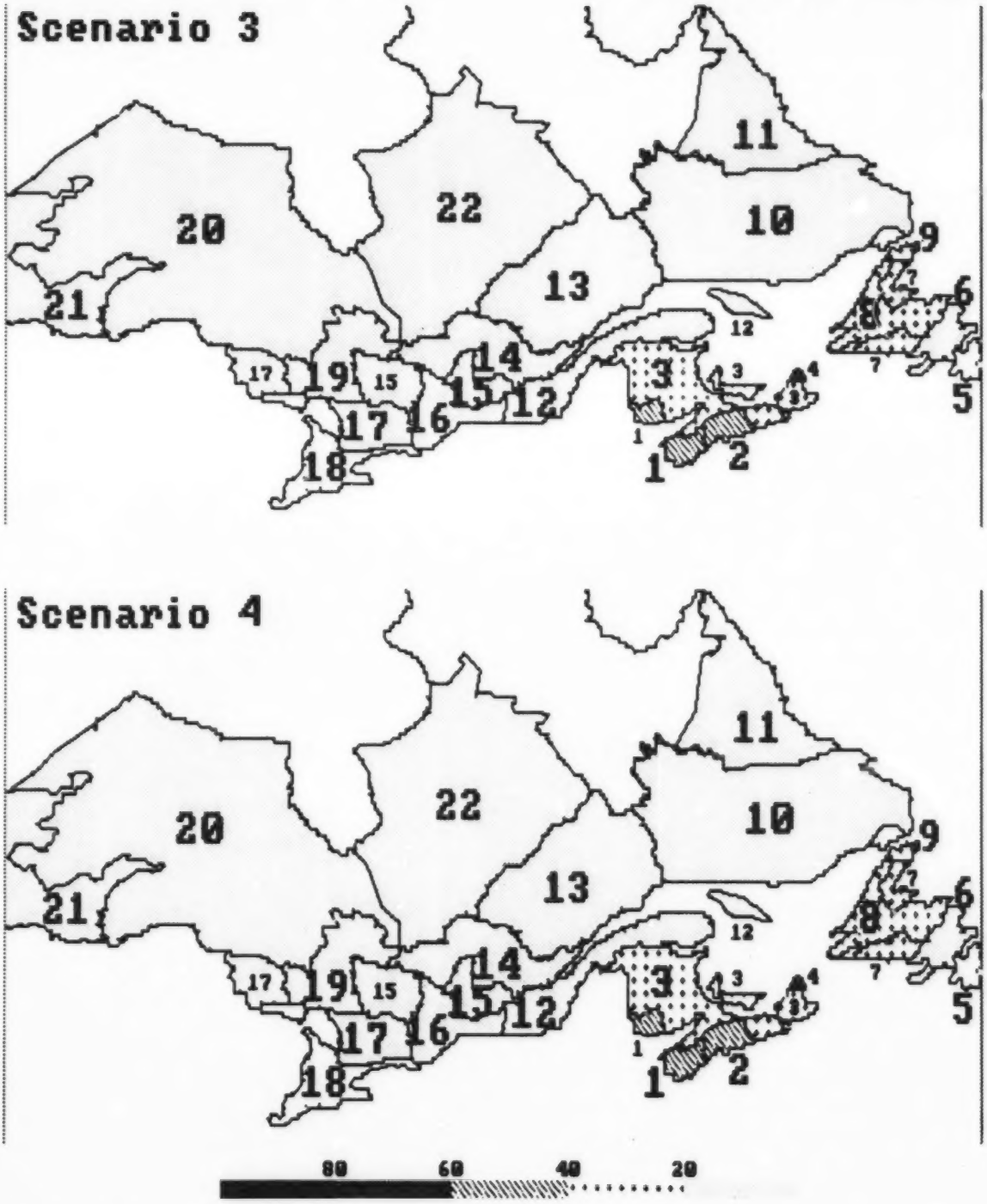


Figure 4.3.7: continued.

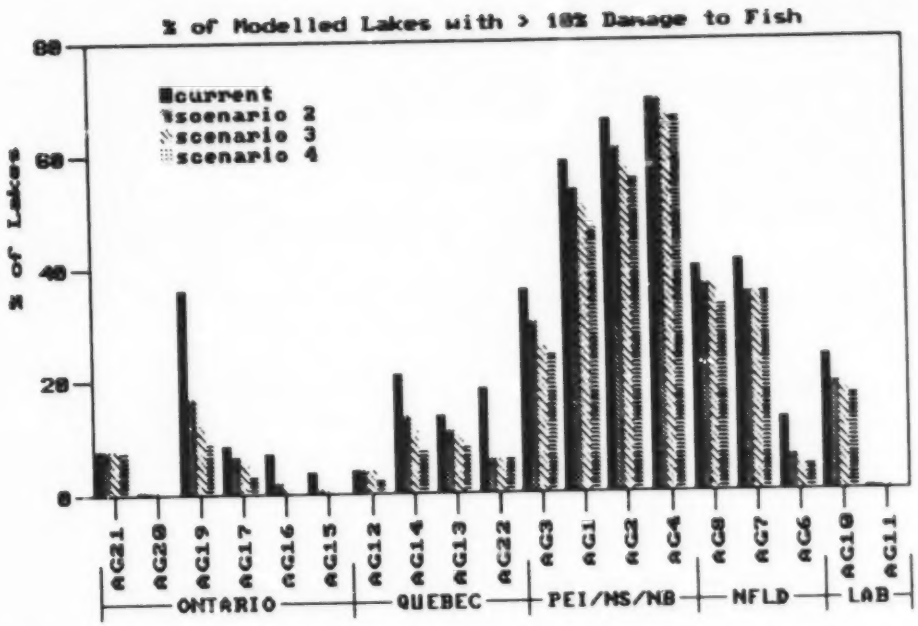


Figure 4.3.8: Predicted percent of modelled lakes in each AG exceeding the fish damage level (i.e. ≥10 % reduction in species richness) for the 4 deposition Scenarios specified in Section 4.3.2.

For example, the percentage of lakes exceeding the fish damage level are predicted to be 59%, 54%, 51%, and 47% for the 4 deposition Scenarios respectively for AG 1 (southern Nova Scotia - New Brunswick), while the change is less (36%, 30%, 26% and 25%) for AG 3 (northern Nova Scotia - New Brunswick). For AG 12 (St. Lawrence S. Shore), the damage level is negligible for all Scenarios as the lakes are protected by well buffered soils. These 3 AGs are geographically very close to each other; the large variations in the fish species response indicate that biological damages are influenced more by terrain characteristics that contribute to lake ANC than by SO_4^{2-} deposition. Comparison of Figures 4.3.8 and 4.3.6a shows that the predicted percent of lakes exceeding the fish damage level conforms well to that for the excess percent pH<6, thereby lending support to the use of a pH=6 chemical threshold for estimating biotic damage. However, recall that for some AGs, the quantity of data used to determine biological damage was greater than that used to determine excess percent pH<6, the latter having excluded all lakes with historical pH≤6.

The data for the AGs have been grouped into 3 larger regions to demonstrate the gross differences that exist in fish damage across eastern Canada resulting from the 4 deposition Scenarios (Figure 4.3.9). For the whole of eastern Canada, the damage level decreases from about 17% of sampled lakes exceeding the fish damage level to about

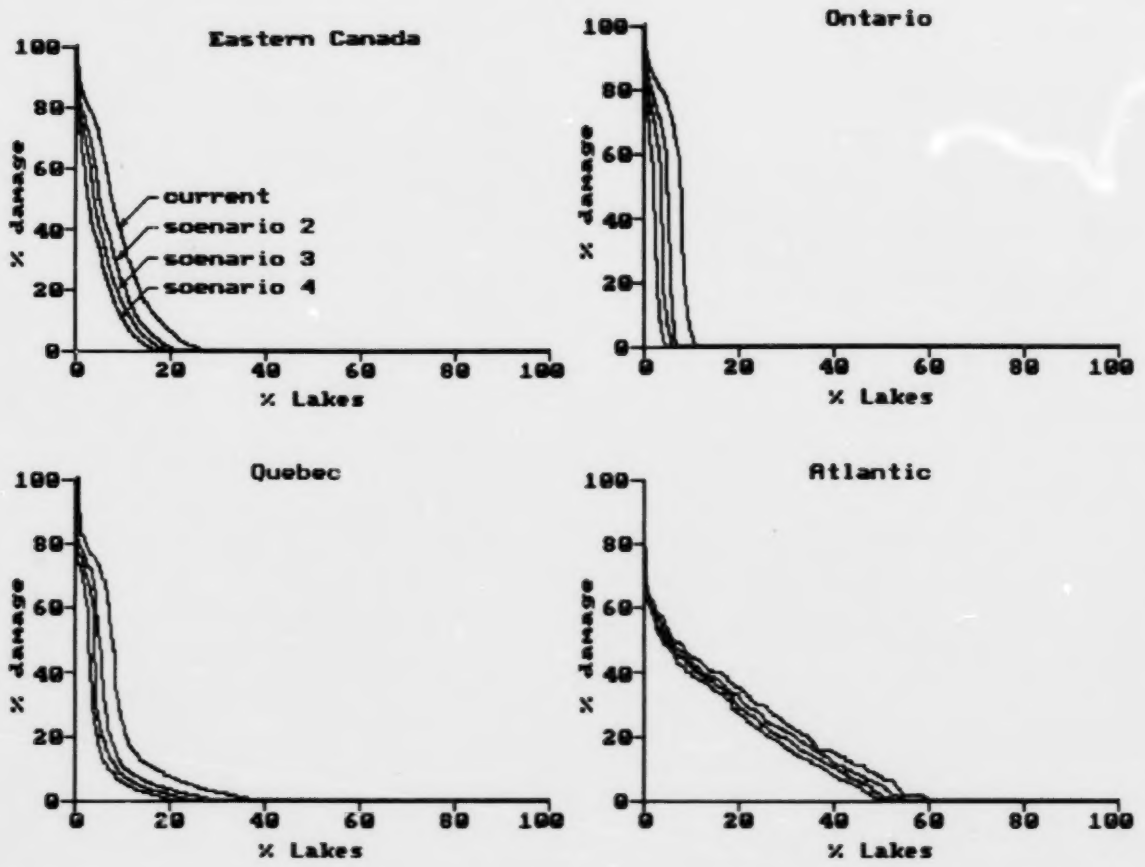


Figure 4.3.9: Predicted percent reduction in fish species richness for differing portions of eastern Canada under the 4 SO_4^{2-} deposition Scenarios.

10%, when the deposition is reduced from the current level (1982-1986) to the Scenario 4 level. There are regional differences within eastern Canada, as explained above. For example, Figure 4.3.9 shows that for Ontario, the percentage of lakes exceeding the fish damage level decreases from about 9% to 3% for the same change in the deposition, while for Québec, the decrease is from 16% to 6%. For the Atlantic region, it changes from 46% to 37%; clearly this region receives the least benefit from the planned and proposed emission control programs. The critical SO_4^{2-} load needed for each AG to achieve a pH>6 is presented in Section 4.2.3.

As with the chemical model, the biological model used is subject to uncertainties in the data and model formulations. Since it is not possible to verify the biological model, we compare the Matuszek et al model results discussed above to those computed by another biological model (see Section 4.3.1.2). Because the Minns et al model has a more conservative lethal threshold, it tends to predict a higher level of fish species

damage than the Matuszek et al model (Figure 4.3.2). For example, the percentage of lakes exceeding the fish damage level predicted by the Minns et al model for the current loading is about 16% for Ontario. For Scenario 4, it becomes 6% (compare to results in Figure 4.3.9). Probably, the true answer lies somewhere between the two model results.

4.3.6 TIME-DEPENDENT WATER CHEMISTRY MODELLING

The rate of chemical change and time required to reach a steady-state concentration for a given acid load differs from lake to lake. Theoretically, estimates of watershed response time ranges from decades to centuries (Arp and Ramnarine 1983; Cosby et al 1985; Davis and Goldstein 1988; Ormerod et al 1990); however, accurate data that can be used for calibrating or verifying these theoretical response times are not available.

Several process-oriented mathematical models have been developed that simulate temporal chemical responses of surface waters, e.g. the Turkey-Mersey Watershed Acidification Model (TMWAM; Lam et al 1988; Bobba and Lam 1988), the ILWAS model (Chen et al 1983), the Watershed Acidification Model (WAM; Booty 1983; Booty and Kramer 1984), the Birkenes model (Christophersen et al 1982; Beck et al 1987), the Extended Trickle-Down Model (ETD; Schnoor et al 1987), the MAGIC model (Cosby et al 1986; Jenkins and Cosby 1988) and the RAINS model (Kamari 1985). The ETD, MAGIC, and ILWAS models have been used to estimate the recovery times of selected lakes in the U.S.A. (US EPA 1985), and the RAINS model was considered for a similar exercise in Europe. Given the limitation of reliable data and knowledge of the temporal processes (Neal et al 1987, 1988), it is difficult to provide accurate estimates of chemical recovery rates prompted by changes in deposition. At this stage, it is better to examine the accuracy of a number of these models by comparing their predictions when applied to a common data base. As a case study, MAGIC was applied to data from the Turkey Lakes Watershed (TLW) in central Ontario to give long-term (50-100 year) predictions, while differences in model performances over the short term (2-4 years) were evaluated by applying TMWAM, ETD, ILWAS and RAINS to the same data. Modelling of episodic acidification is also considered briefly.

4.3.6.1 APPLICATION OF MODELS TO THE TURKEY LAKES WATERSHED

4.3.6.1.1 Long Term Simulation

The MAGIC model has been applied to the headwater of the TLW (Batchawana Lake, see Jeffries et al 1988) in order to evaluate the long term trends due to constant SO_4^{2-} deposition and loadings that vary according to Scenarios 2, 3, and 4 as defined in Section 4.3.2. MAGIC predicts that under constant deposition (27.8 $kg.ha^{-1}.yr^{-1}$), lake outlet pH will be reduced by 1.2 units and ANC by 185 $\mu eq.L^{-1}$ by the year 2124 (Figure 4.3.10). When the SO_4^{2-} input is reduced according to the Scenarios (varying from 27.8 for the current Scenario to 15.8 $kg.ha^{-1}.yr^{-1}$ for Scenario 4), the model predicts chemical responses that differ from the constant load Scenario (Figure 4.3.10), i.e. by the year 2124, the pH has decreased by only 0.4 pH units and the ANC by only 97 $\mu eq.L^{-1}$. The benefits of deposition reduction (higher pH and ANC) are almost immediately apparent

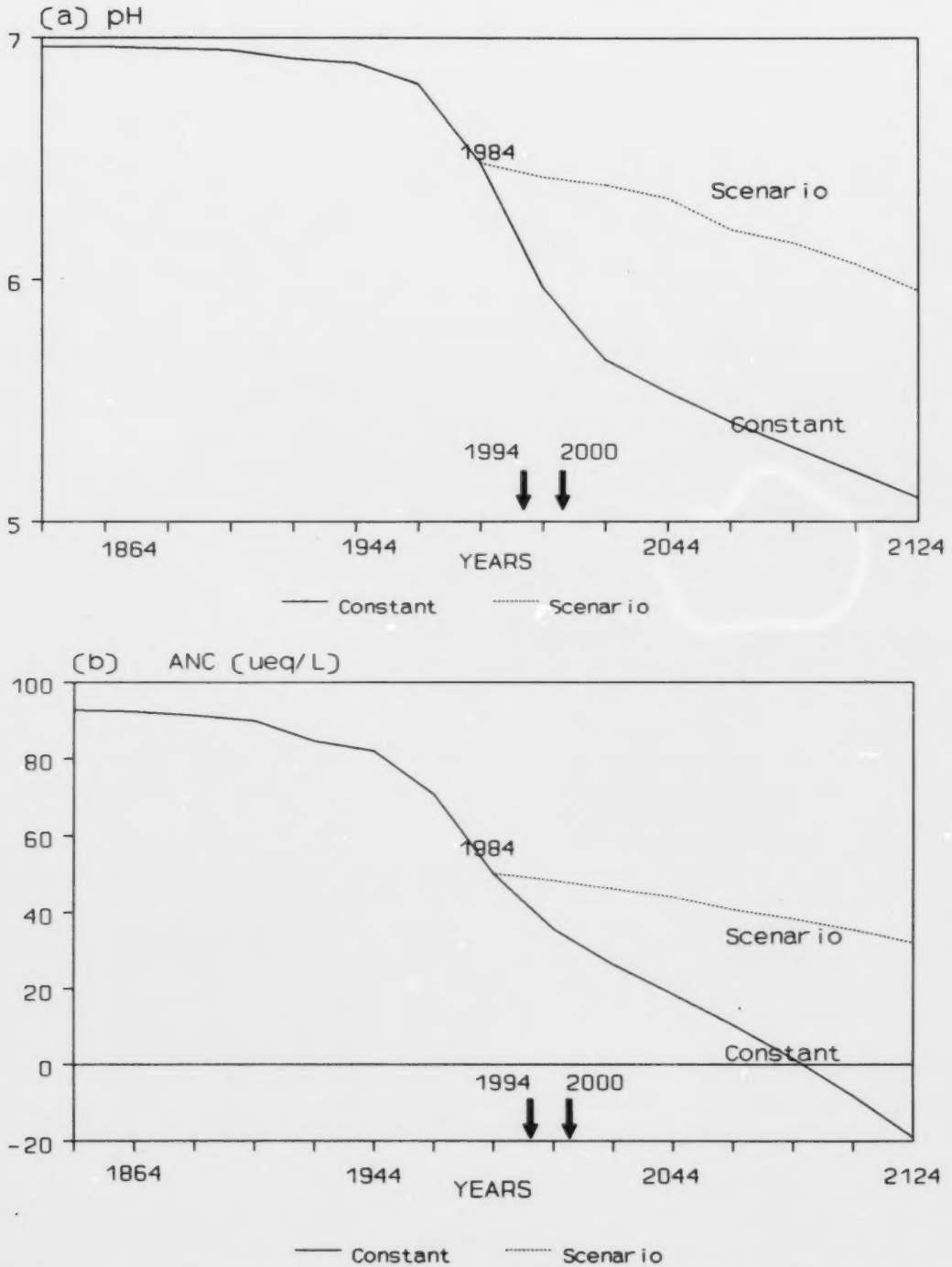


Figure 4.3.10: MAGIC Model predictions of (a) pH and (b) ANC for Batchawana Lake outflow (TLW) under constant and varying SO_4^{2-} deposition Scenarios (see text).

due to the asymptotic nature of the chemical response.

Some of the parameters used in the MAGIC model may exhibit a significant degree of heterogeneity within a watershed. For example, the MAGIC parameter EMX (maximum soil SO_4^{2-} adsorption capacity) for the TLW has not been thoroughly measured. Foster (1985) examined 13 B horizons in 5 soil profiles within a small area of the TLW and found that the greatest adsorption was 40 ppm SO_4^{2-}-S, and 3 samples adsorbed no SO_4^{2-} at all. A sensitivity analysis was performed in which the value of EMX was varied from 25 to 100 $\mu eq.g^{-1}$ for a constant SO_4^{2-} load 27.8 $kg.ha^{-1}.yr^{-1}$; the effect on the outlet stream pH for Batchawana Lake is shown in Figure 4.3.11a. Figure 4.3.11b gives the results for the reduced input Scenarios. For constant input, MAGIC predicts that it would take 58 years longer for the system to acidify to pH=5.5 if the value of EMX was 100 rather than 25 $\mu eq.g^{-1}$; similarly, under reduced deposition, it predicts that it would take 70 years longer for the system to acidify to pH=6.5 for the 2 EMX values. Clearly, the uncertainties implied by these results must be considered when applying MAGIC to large areas where significant variations in model parameters may exist.

4.3.6.1.2 Short Term Simulation

The ILWAS, RAINS, ETD, and TMWAM models were applied to Batchawana Lake in the TLW in order to evaluate and compare the accuracy of the model predictions of seasonal variations in pH and ANC. All of the models, except ILWAS, were applied for the period January, 1981 to December, 1984; ILWAS could only be run from January, 1983 since input data were insufficient for 1981 and 1982. The models used common input deposition and meteorology. Monthly averaged pH and ANC simulations as well as observed data are presented in Figure 4.3.12. The models give differing simulations of water chemistry. Monthly predictions were compared to the observed data using the coefficient of efficiency (E, a measure of the improvement of variance over the mean-as-model, Nash and Sutcliffe 1970), correlation coefficient (r), and regression slope (s). This analysis showed that TMWAM provided a slightly better simulation of pH (E=0.26, r=0.64, s=0.65) than ETD, while ETD was superior for predicting ANC (E=0.61, r=0.78, s=0.96). The RAINS model was least effective for both chemical variables, and in fact, was not an improvement over a mean-as-model simulation. The ILWAS model could not be included in the intercomparison since it was only run for the final 2 years. However from Figure 4.3.12, it is obvious that it tended to overpredict the fluctuations of ANC more than the ETD and TMWAM models but much less than RAINS. It provided better predictions of pH fluctuations (both in magnitude and timing) than either ETD or RAINS.

Watershed acidification models used to assess long term responses are very difficult to verify. Strict validation of these types of models requires long time series data records to determine whether the model estimates match the observed; unfortunately, very few, if any, such records exist for most areas. Therefore, the question of whether the long-term responses estimated by models are projections of real responses remains uncertain. All but 1 of the 4 models applied to the TLW have predicted monthly or seasonal fluctuations in the acidity that are within reasonable ranges of accuracy.

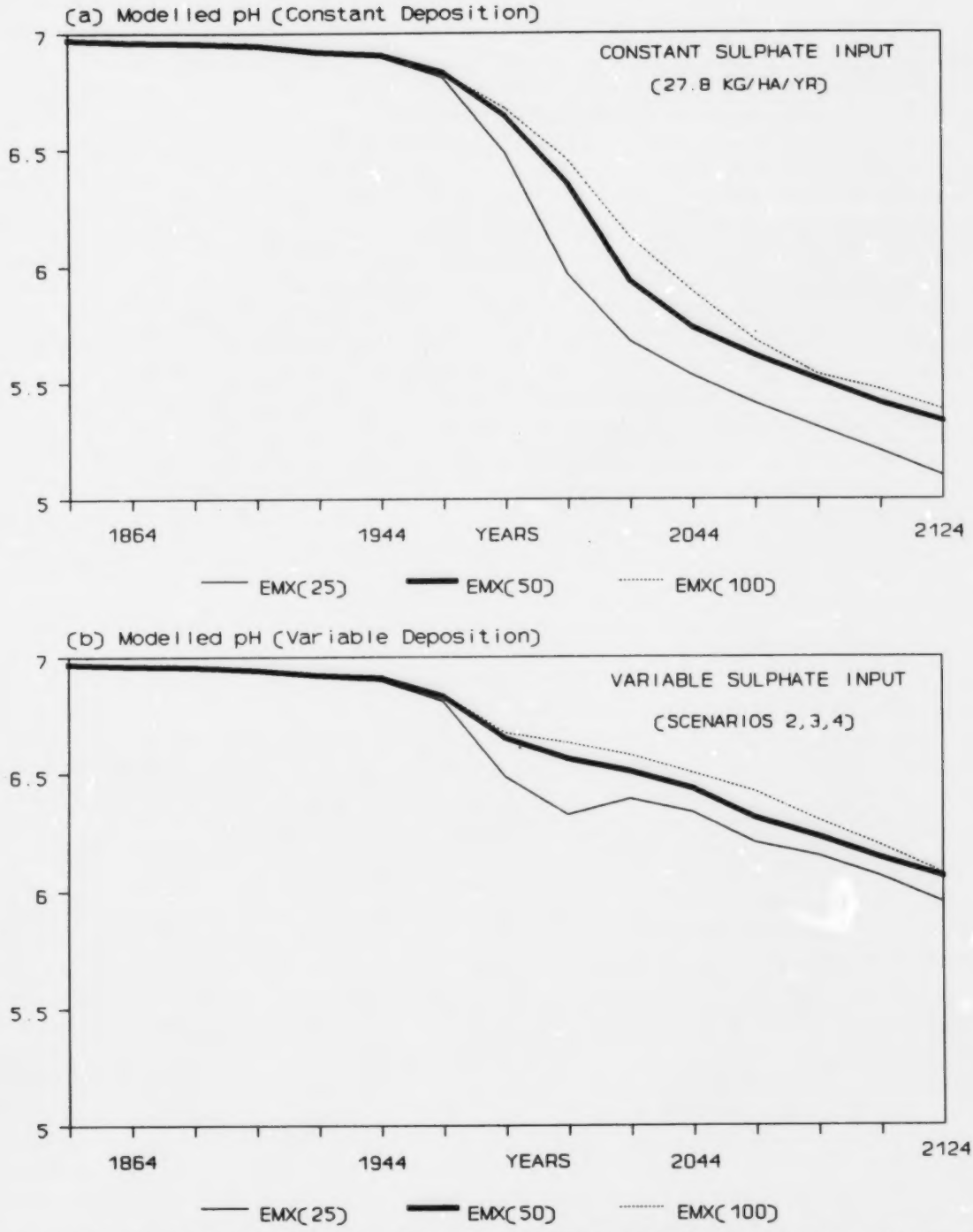


Figure 4.3.11: Variation of pH predicted by MAGIC for Batchawana Lake outflow for 3 values of the model parameter EMX for (a) constant and (b) varying SO_4^{2-} deposition (see text).

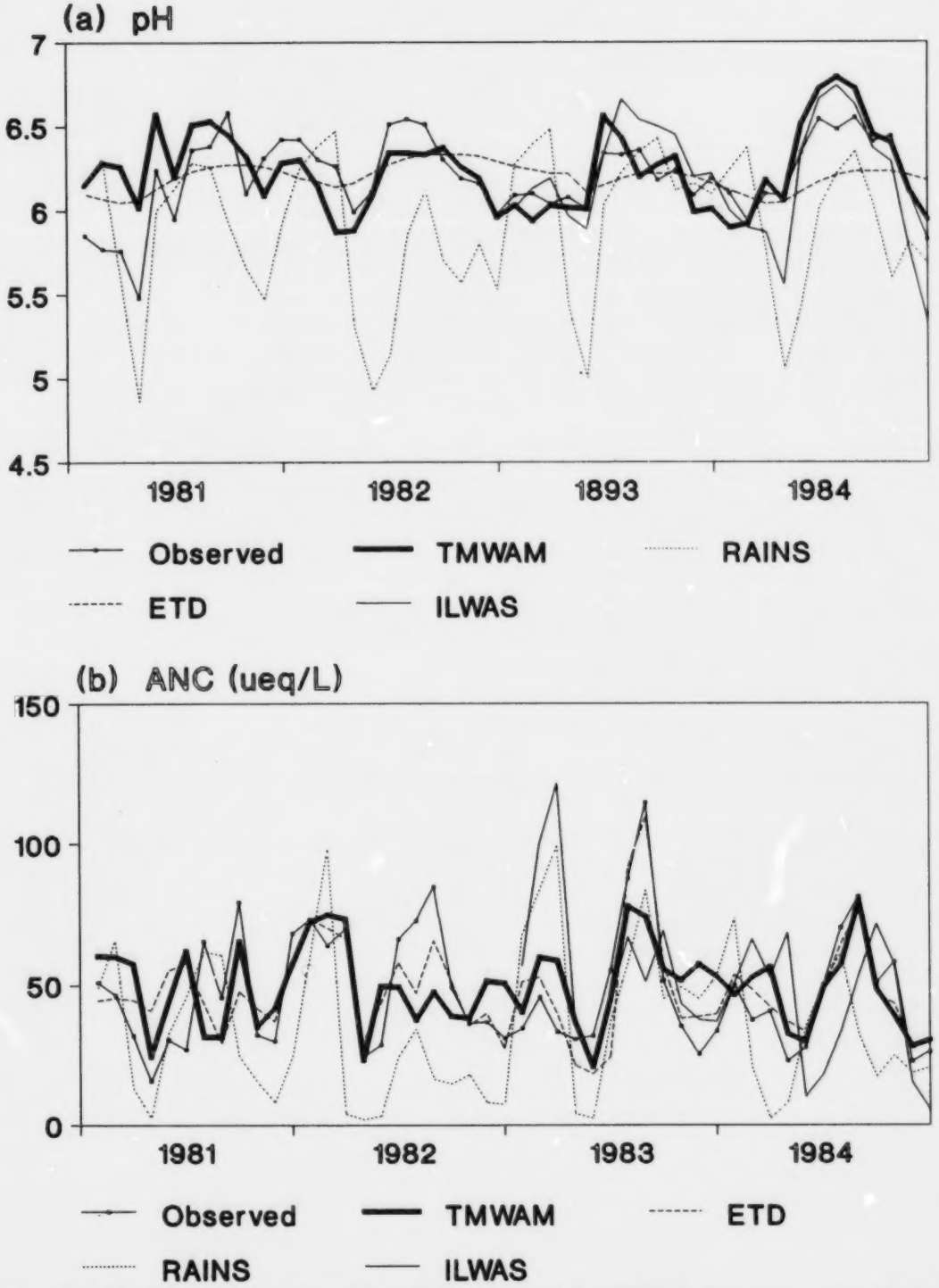


Figure 4.3.12: Observed and predicted (a) pH and (b) ANC at Batchawana Lake outlet from 1981 to 1984 (predictions from the TMWAM, ETD, ILWAS, and RAINS models).

4.3.6.2 MODELLING EPISODIC ACIDIFICATION

As shown in Figure 4.3.12, pH depressions >0.5 units often occur in the TLW, particularly during snowmelt. Observations of episodic acidification have been presented earlier (Section 4.1a.8). Statistically, the magnitude, duration, frequency and timing of acidification episodes can be related to hydrological events using the method of Waylen (1981). The probability of acidification episodes defined as pH<6 in Batchawana Lakes (TLW), and pH<5 in the Mersey River (southern Nova Scotia) is shown in Figure 4.3.13. The differing definition of an episode reflects the differing terrain characteristics and water chemistry present in these areas. There is a maximum of 3 acidification events per year, as indicated by a maximum PE (Probability of Events) of 3, for both areas. The probability of duration of an episode was assessed also (Figure 4.3.14), and it can be seen, for example, that 50% of them last <15 days in the TLW, but in the Mersey River, 50% last about 35 days.

4.3.6.3 RECENT APPLICATION OF MODELS TO OTHER CANADIAN LOCATIONS

To date, the acidification models have been applied to only a few locations in Canada. The Mersey River and Moose Pit Brook in southern Nova Scotia are affected by both naturally occurring organic acidity and SO_4^{2-} deposition (Kerekes et al 1986). Intermittent snowmelt episodes often complicate analysis of seasonal variability in water chemistry (Howell 1989; Freedman and Clair 1987). Clair et al (1989b) also found seasonal changes in the pK coefficients for organic acids. Lam et al (1989) have applied the TMWAM model to both river systems and successfully simulated most of the seasonal changes in chemistry observed during 1983-1985. Using the technique of Rustad et al (1986), Lam et al (1989) also estimated that, because of differences in organic acidity, the mean pH for the Mersey River will increased from 4.99 to 5.38 if the stream SO_4^{2-} is reduced by 50%, while Moose Pit Brook will increase only from 4.64 to 4.82. Confirmation of these predictions depends on better organic anion measurements (Bourbonniere et al 1989) and modelling (Clair and Kramer, submitted).

The Birkenes Model (Rustad et al 1986) was modified to include an organic acid component, and when applied to a tributary of Harp Lake (south-central Ontario), successfully simulated variations in water chemistry including snowmelt episodes. Model analysis indicated that a 50% reduction of stream SO_4^{2-} causes a pH increase of 0.17-0.47 units (average = 0.32) which is similar to the Mersey River case.

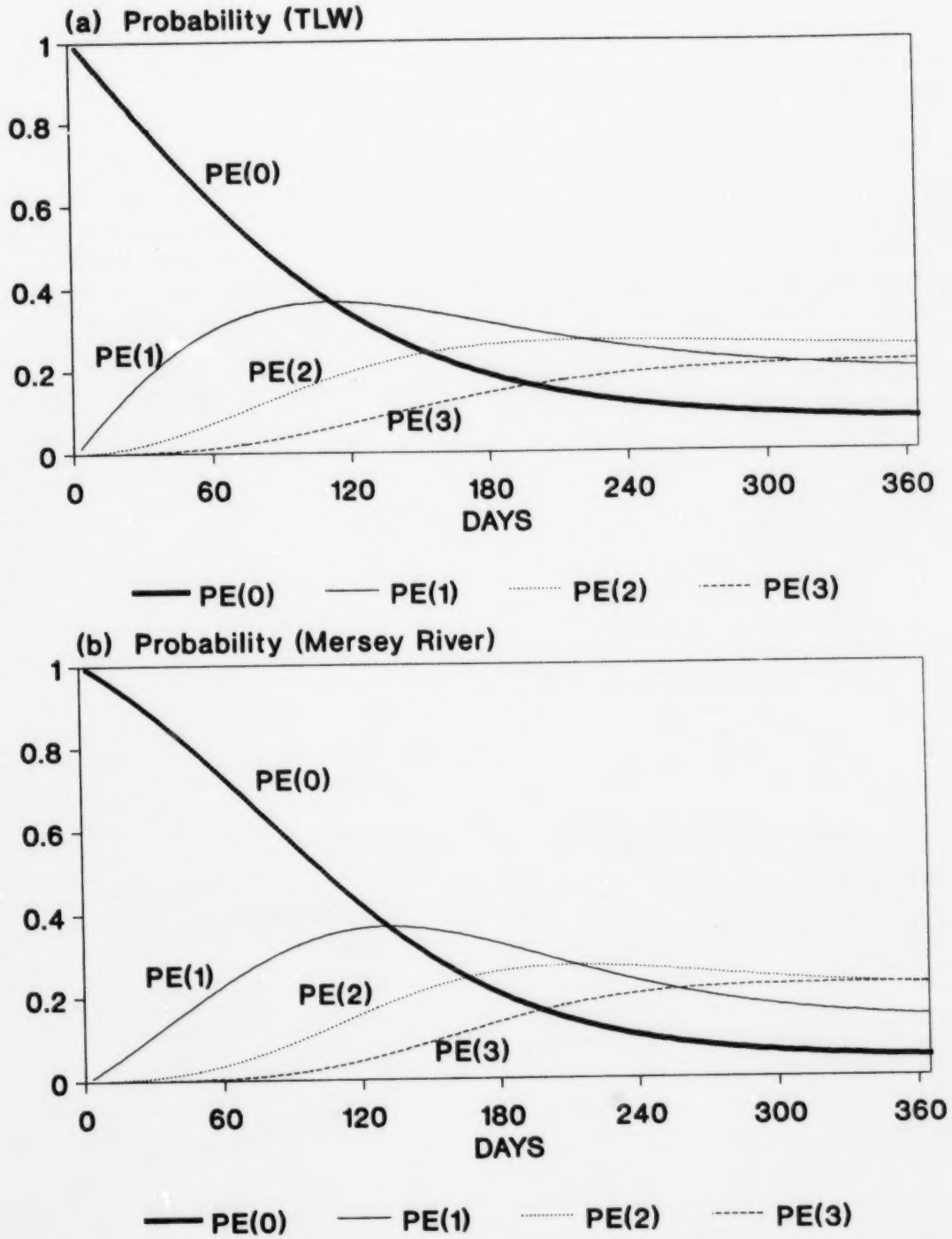


Figure 4.3.13: Probability of 0, 1, 2, or 3 periods of episodic acidification occurring each year in (a) the TLW (pH<6), and (b) the Mersey River (pH<5) using the method of Waylen (1981).

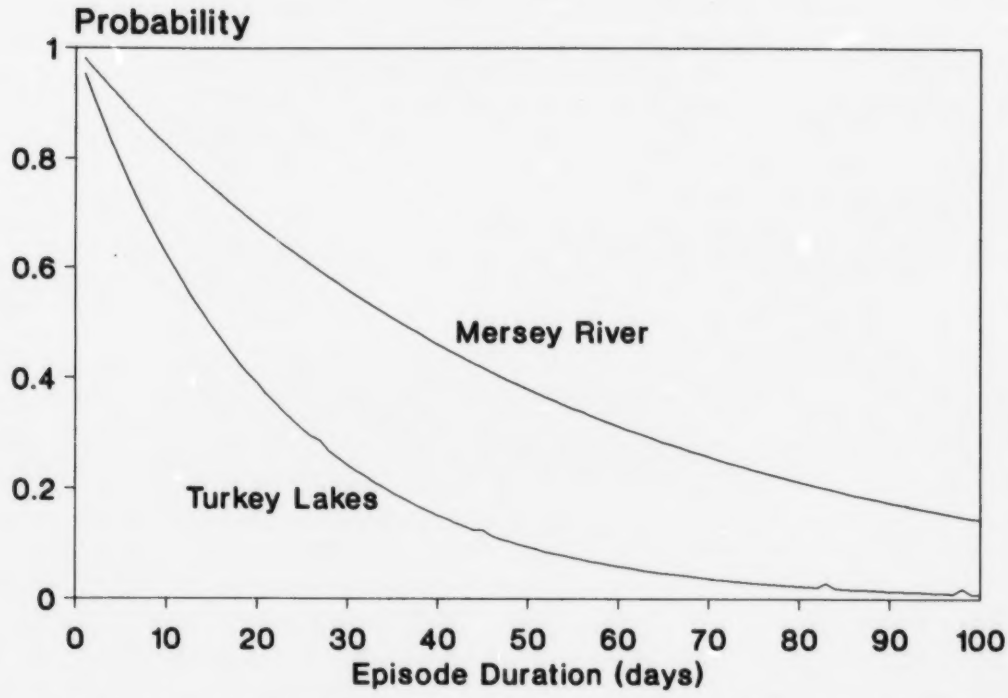


Figure 4.3.14: Duration probability of episodic acidification in the TLW and Mersey River; pH thresholds defining an episode are specified in the text.

4.4 WHAT ARE THE POTENTIAL SHORT-TERM MITIGATIVE MEASURES, THEIR LIKELY CONSEQUENCES AND ANTICIPATED SUCCESS?

Summary: The most common approach for mitigating the impact of acidification of inland surface waters on the fishery resources is the application of limestone or other alkaline materials to lakes and rivers to neutralize the acid input. Neutralization or "liming" has been used extensively to treat the symptoms of acidification in Scandinavia (Bengtsson et al 1984, Rosseland and Hindar 1988). Liming is also in use in the United States, with both operational and experimental programs in place (Porcella 1989, Schofield et al 1986). In Canada, experimental liming is being employed at a few sites and has proven effective for the preservation of a wild indigenous strain of Atlantic salmon and the restoration of a reproducing lake trout population. However, the increased pH and ANC that result from liming are temporary effects, and continuous reapplication is required as long as the lakes and streams continue to receive acidic deposition. The "success" of liming experiments should not discourage efforts to control industrial emissions of SO_2 since it is the only reasonable long-term solution. Other amelioration approaches, such as use of hatchery reared fish, may also be useful in some instances but do not correct the cause of the ;problem.

4.4.1 NEUTRALIZATION EXPERIMENTS IN CANADA

4.4.1.1 ONTARIO - SUDBURY LAKES

Neutralization experiments involving acid and metal contaminated (Cu, Ni, Zn) lakes near the smelters at Sudbury have shown that water quality improvements may be short lived and that metal concentrations remain at levels toxic to most biota, especially fish (Yan and Dillon 1984). Liming of Bowland Lake, a lake outside of the area of high metal deposition, increased the pH from 5.0 to 6.7 and caused a decline in Al concentrations from 130 to 30 $\mu g.L^{-1}$ (Molot et al 1990a). Although runoff water during snowmelt continued to produce pH depressions in the nearshore areas of Bowland Lake, reintroduced lake trout survived, grew, and reproduced in the limed lake (Gunn et al in press). Some positive responses were observed also in phytoplankton (Molot et al 1990b), zoobenthos (Keller et al in press), and filamentous algae (Jackson et al in press).

4.4.1.2 QUEBEC - BROOK TROUT LAKES

Eight lakes near Mauricie National Park, Québec ranging in pH from 5.0 to 6.1 were limed and stocked with brook trout to improve the yield to anglers (Houde et al 1989). Winter liming produced low initial dissolution rates but the efficiencies increased with time, eventually, reaching levels similar (70%) to those achieved more quickly by summer liming. Angling yields were higher in limed lakes than in nearby unlimed lakes, but this effect was independent of whether or not the lakes were acidic before liming.

4.4.1.3 NOVA SCOTIA - ATLANTIC SALMON RIVERS

White et al (1984), Watt et al (1984) and Watt (1986) evaluated several different methods (river dosers, instream limestone gravel and headwater lake treatment) of liming salmon streams, and concluded that liming the headwater lakes was the most practicable and economical method to achieve a short term restoration of acidified salmon habitat in Nova Scotia. The limed lakes release ANC to the downstream habitat, and compensation for freshets is automatic. The lakes are limed in winter to prevent layers of low pH runoff from forming at the lakes' surfaces during the winter. The major disadvantage is that most Nova Scotian lakes have a turnover time of less than one year, hence annual liming is required.

In the East River experiment, the objective was one of "genetic salvage", to test the practicality of preserving a native wild Atlantic salmon stock within a deacidified refuge (Watt et al in prep). About 400 tonnes of lime were spread annually on the ice of headwater lakes draining into the East River. Population densities of salmon fry in the river were close to zero before liming and usually were significantly higher after liming. The population density of fry increased in the summer of 1989, to the highest population density recorded anywhere in East River since the study was started. Neither the distribution nor the densities of brook trout and American eels has shown any evident response to liming. Common white sucker, lake chub and banded killifish show no change in population densities, but these species were found at more sites in the limed portion of the river after the liming was started than before.

Sangalang and Freeman (1987), Freeman et al (1989) and Sangalang et al (submitted) held feeding adult Atlantic salmon in cages, during the reproductive season to test the physiological effects of liming. Prior to liming, the salmon held in at low pH (4.7-5.1) gained less weight, suffered higher mortalities, and showed abnormal sex and corticoid hormone development compared with fish held in higher pH (5.3-5.8). Significant differences were found in gill histology and morphometry, plasma glucose levels, plasma, liver and muscle electrolyte levels, bone and thyroid hormone changes, and changes in liver enzyme levels (Brown et al submitted; Harvey et al submitted; Majewski et al submitted; Jagoe and Haines submitted; Wesson et al submitted; and Willis et al in press). Liming the lower pH water reversed these effects, but did not entirely eliminate all of them.

4.4.2 OTHER MITIGATION APPROACHES

Vulnerable juvenile stages can be reared in a protected hatchery environment and then planted as catchable trout in lakes (Houde et al 1989) or as Atlantic salmon smolts ready to go to sea (Anon. 1988). Canada has been able to replace 10-15% of the Atlantic salmon production lost to acid rain by using the excess rearing capacity already available in hatcheries, at a cost of about $100 per landed fish (Watt 1988). This is one-half the cost of liming. Building new hatcheries for more extensive stocking would, however, cost as much as liming. The Department of Fisheries and Oceans has stocked 1.7 million Atlantic salmon smolts into acidified Nova Scotian rivers since 1980.

Stocking of acid-tolerant fish is another alternative to habitat rehabilitation. Rahel (1983), Schorn (1986) and Hurley et al (in prep) have shown that different strains of fish within the same species differ in acid tolerance. Acid resistant strains have been stocked in the Adirondack lakes in New York State (Simonin et al 1988), but an evaluation of the program concluded that even acid resistant strains (brook trout) were not likely to survive in the more acidic lakes of the region.

4.5 WHAT ARE THE MOST URGENT KNOWLEDGE GAPS AND NEW RESEARCH DIRECTIONS?

Research into the structure and function of aquatic ecosystems and monitoring of their chemical and biological characteristics over the last decade has produced the information base required to present this Assessment. While understanding of the ecological consequences of acidic deposition has advanced greatly, production of the Assessment has shown that there are still several knowledge gaps that limit or prevent drawing quantitative conclusions on cause-effect relationships. The research needs that arise from these gaps can be grouped within the following 5 general categories. Since many of the activities noted below are interdependent, it is not possible to assign specific priority.

Data Analyses

Further analyses of data collected over the last decade will improve quantitative knowledge of the spatial extent and degree of aquatic acidification effects. This includes: statistical extrapolation of available sample information for lake chemistry to the overall population in eastern Canada, development of acidification indices and linkage to information on biological status, development of ecological thresholds expressed in terms of ANC rather than PCO_2 equilibrated pH, assessment of the stream and river database, further refinement of the correlative relationships between terrain characteristics and aquatic chemistry, and a more in-depth analysis of data with a focus on the acidifying effects of N deposition. Efforts should also be directed to development of new ways to measure organic acidity or organic anion concentration in order to improve knowledge of their specific contribution to the total acidity of surface waters. Information on biomass and/or fisheries yield should be developed from existing biological databases so that it can be incorporated into models predicting biological effects.

Surveys

Small lakes (< 1 ha) make up a large proportion of the Canadian lake resource in terms of numbers and are also important habitat for some aquatic species. Yet, almost no information exists on their chemical and biological status. Surveys conducted over the next 5 years to close this knowledge gap may include a statistically designed lake selection criterion (applied over a limited locale only) to test model-based statistical extrapolations from sample information. Data collection to address effects related to N deposition and metal mobilization needs a greater priority than in the past. Surveys to fill gaps in knowledge for western Canadian waters and groundwaters in general are indicated.

Monitoring

Data obtained from long-term monitoring remain as the only unequivocal means for validating acidification models, measuring the ecological response to emission control programs, and quantifying the natural episodic and seasonal variability present in aquatic systems. It is essential that existing long-term monitoring activities (now approximately

one decade old) be maintained in perpetuity. The information base available for assessing the rate and extent of biological response to decreasing water acidity is minimal. Further documemtation of the sequence and rate of biotic recovery is essential including evaluation of secondary effects related to interaction between species. Further research is warranted to define the effects on wildlife.

A significant component of long-term monitoring is best conducted within a whole-ecosystem context (sometimes called "integrated monitoring"), in which all aspects of the climatic, hydrological, geochemical, and biological properties of a catchment are followed in order to deduce the processes the control ecosystem response. Existing research and monitoring activities of this type must be maintained and enhanced. The knowledge obtained has benefits well beyond LRTAP aquatic effects. There is a need to have a direct and acknowledged tie between these activities and contaminant (metals, toxic organics, etc.) research programs to permit evaluation of the relative proportion of biotic damage caused by the different pollutants. Research to better understand the inter-relationship between acidity and other contaminants (e.g. Hg) is also advised. Development of predictive models require such information bases. Enhancement of the still meagre knowledge of biological effects of episodic acidification is most conveniently pursued at these monitoring sites. Comprehension of the relationship between the terrestrial and aquatic components of the ecosystem is key, and research to further quantify terrestrial/aquatic linkages is warranted.

Wetlands

Wetlands form important habitat for many species (particularly birds) and their response to acidic deposition differs from most lakes. Further knowledge is required on the importance of wetland storage and release of S and N, and the effect of deposition on wetland production of DOC. In addition, wetlands should be incorporated the monitoring program. The development of a geographically referenced wetland database for eastern Canada is important.

Modelling

Models should be refined or new ones developed in order to better predict the effects of SO_2 and NO_x emission reductions on aquatic chemistry and biota. Hence modelling needs include: incorporation of N into water chemistry models, improvements in the prediction of the effects of natural organic acidity, further development of biological damage models, and improvements in the determination of critical loads. Validation of existing models with the ever-lengthening monitoring data is always a priority. This effort coupled to an improvement in our knowledge of the biogeochemical mechanisms regulating water chemistry will improve the precision of model predictions and the accuracy of assessing acidification reversibility.

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